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14. ABSTRACT
Remarkable progress was made in developing new compounds with many of the properties required for AFOSR specs. Several of the compounds have high positive heats of formation, densities approaching 2 g/cm3, and apparently low sensitivities. Heterocyclic rings (containing amino, nitro or azido substituents) paired with nitrate, perchlorate, dinitramide, or picrate anions form highly energetic salts which may be more environmentally acceptable (perchlorate excepted). Additionally, high energy salts in which both the cation and anion are high-nitrogen species, e.g., azolium, substituted azolium, guanidinium, bridged imidazolium and triazolium, urotropinium cations, etc. coupled with azolates, substituted azolates, azotetrazolate, bis(5,5'-tetrazolates), iminobis(5-tetrazolate), etc. were synthesized. All have been thoroughly characterized via NMR and mass spectral analyses, melting point, thermal stability, density, and elemental analyses. Gaussian03 and CHEETAH 4.0 gave heats of formation, and detonation pressure/velocity and specific impulse. An accurate empirical method for estimation of densities of energetic compounds was developed.

15. SUBJECT TERMS
energetic salts, heat of formation, density, calculation, stability, high-nitrogen heterocycles, Gaussian, CHEETAH

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3. Objectives: The goal of this research is to develop fundamental understanding of energetic ionic liquids to enable design of materials with desirable characteristics. This goal can be achieved by accomplishing several objectives that include the synthesis and character-ization of a variety of energetic materials having ionic properties. New energetic triazolium and tetrazolium salts will be synthesized. Examples of the new compounds to be obtained through a vigorous synthesis effort include 1,4-dialkyl-3-difluoroamino-1,2,4-triazolium halide that can be synthesized from the electrophilic fluorination and quaternization of the amino-substituted triazole. Metathesis with a silver salt such as silver nitrate forms the nitrate salt. By electrophilic difluoroamination of 1-alkyl-3-nitro-1,2,4-triazole, 1,4-dialkyl-3-nitro-5-difluoroamino-1,2,4-triazolium fluorosulfate will result and an oxidizing anion will be introduced. Nucleophilic difluoroamination of 5-amino-tetrazole with subsequent quaternization will result in 1-difluoroamino-4-alkyl-5-amino-tetrazolium halide whose anion will be exchanged. The energetics of these salts is determined by the nature of both the anion and the cation. Each of the new compounds will be characterized spectroscopically and by elemental analysis. Physical properties including melting point, viscosity, density, thermal stability (DSC and TGA) and qualitative impact sensitivity will be measured. These results will guide the synthetic work allowing the right decisions to be made based on the effectiveness of cation substituents and the oxidizing ability of the anion in providing ionic liquids with the appropriate physical and chemical properties.

4. Status of effort: The current award became effective on April 1, 2003. Our research efforts have been reported in 56 publications in the reviewed technical literature.[1-56] During this period, a large number of substituted oxazolidinium, morpholinium, imidazolium, diazolium, pyridazinium, pyrazinium, guanidinium, triazolium, tetrazolium, bitriazolium, bi(triazolium) amine, bis(imidazolium) methane, bis(triazolium) methane, substituted diazolate, substituted triazolate, substituted tetrazolate,

azotetrazolate, imino-tetrazolate, bis(tetrazolate), picrate, nitrate, perchlorate, dinitroamide, and trinitroimidazolate salts were synthesized and characterized (*vide infra)*. During the second year, we added markedly to our instrumentation which permitted fuller characterization of our new compounds. During the third reporting period, because of the risk in shipping samples for elemental analyses, we added a CH and N analyzer to our instrument pool. Thus, we were closer to being able to determine most of the properties necessary for AFOSR specs including sensitivity measurements with the addition of a Bam Fallhammer apparatus. Programs for G3 and Cheetah calculations were also acquired and utilized in predicting properties prior to synthesis. Remarkable progress in developing new compounds with many of the required properties was made. Several of the compounds have quite high positive heats of formation and higher densities, and meet many of the other desired criteria as well. These accomplishments are summarized below.

5. Accomplishments/New Findings:

a. Syntheses and Thermal Properties of Quaternary Oxazolidinium/ Morpholinium Salts[13]

No thermodynamic data are available for the oxazolidinium (**1-3**) and the morpholinium (**4-7**) perchlorates and nitrates but it should be noted that each of these salts (**1-7**) melts <100 °C and some have T_gs (phase transition temperatures) <-78 °C. With the exception of **3**, they are thermally stable to > 250 °C. Densities of **1, 2,** and **5** are ~1.50 g/cm^3 (Scheme 1, Table 1).

Scheme 1

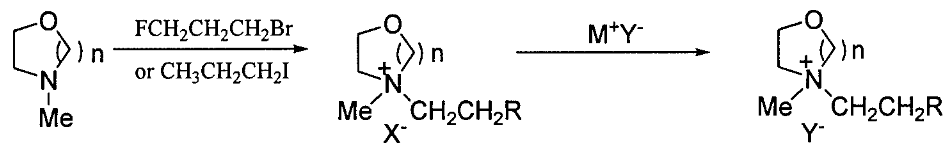
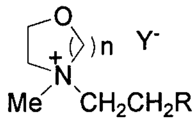


Table 1. Structures and Thermal Properties of Quaternary Oxazolidinium (n = 1)/Morpholinium (n = 2) Salts



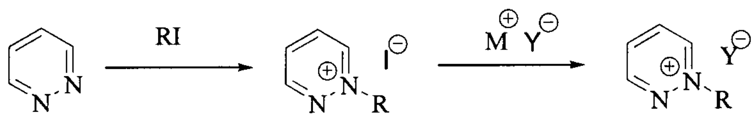
Cpd	n	R	Y	T_m (T_g)[a]	T_d[b]	d[c]
1	1	CH_2F	NO_3	(< -78)	245	1.49
2	1	CH_2F	ClO_4	(< -78)	268	1.46
3	1	CH_3	NO_3	(-60)	183	-
4	2	CH_2F	NO_3	58	289	-
5	2	CH_2F	ClO_4	(< -78)	276	1.50
6	2	CH_3	NO_3	58	285	-
7	2	CH_3	ClO_4	91	312	-

[a] Melting point (T_m), °C; Phase transition point (Tg), °C; [b] Thermal degradation, °C; [c] Measured density using a pycnometer, 25 °C, g/cm^3.

b. Syntheses and Thermal Properties of Quaternary Pyrazinium/Pyradizium Salts.[12]

The 1, 2 or 1, 4 six-membered aromatic perchlorate and nitrate salts (**8-14**) all melt <100 °C and are thermally stable over a range of 155 – 298 °C which is somewhat lower than that for the nonaromatic salts (**1-7**) described in Table 1. The presence of small amounts of fluorine in the substituent arm contributes to the thermal stability and has some positive impact on lowering the melting point (Scheme 2, Table 2).

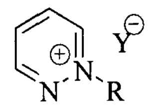
Scheme 2



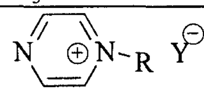
c. Syntheses and Thermal Properties of Quaternary Imidazolium Salts.[22]

Heats of formation were determined for seven of the new substituted imidazolium salts (**23, 24, 30, 31, 32, 34, 35**). Interestingly, while the 5-nitro perchlorate and nitrate salts (**23, 24**) have quite high negative heats, the 2-azido salts (**34, 35**) have modestly high positive ΔH_fs but rather high T_m values. Not surprisingly, **34** (perchlorate) has a positive ΔH_f that is ~3.5 times larger than **35** (nitrate). Unfortunately, the melting points are >100 °C for all of the salts except **20, 24, 26, 29** (MP > 25 °C) and those with 2-n-

Table 2. Structures and Thermal Properties of Quaternary Pyridazinium/ Pyrazinium Salts



Cpd	R	Y^-	T_m [a]	T_d [b]	d [c]
8	n-Pr	ClO_4	16	163	1.54 (1.37[d])
9	n-Pr	NO_3	33	155	1.39 (1.27[d])
10	$(CH_2)_2F$	ClO_4	58	262	-
11	$(CH_2)_2CF_3$	ClO_4	54	298	-
12	$(CH_2)_2CF_3$	NO_3	44	191	-

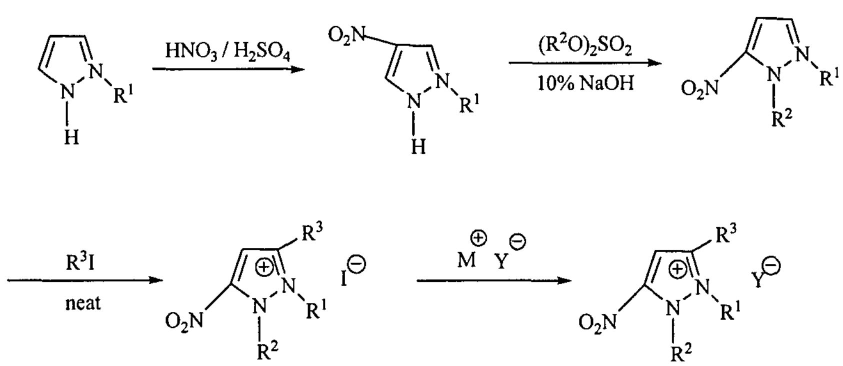


Cpd	R	Y^-	T_m [a]	T_d [b]	d [c]
13	$(CH_2)_2F$	ClO_4	72	157	-
14	$(CH_2)_2CF_3$	ClO_4	102	229	-

[a] Melting point (T_m), °C; [b] Thermal degradation, °C; [c] Calculated density; [d] Measured density using a pycnometer, 25 °C, g/cm^3.

propyl or 2-n-butyl substituents (**30-33**), all of which are liquids at 25 °C. Compounds with positive ΔH_f values (**34, 35**) are highlighted (Scheme 3, Table 3).

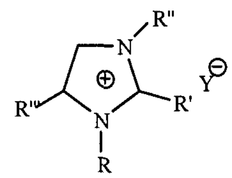
Scheme 3



d. Syntheses and Thermal Properties of Quaternary Triazolium Salts.[19,22]

Of all the triazolium salts synthesized (**36-55**), seven (**41', 41",44, 45, 48, 52, 53'**) are liquids at 25 °C. These are nitrates and all have negative ΔH_fs. Additional salts (**36, 37, 40, 41 43, 47, 50, 51, 53**) with melting points < 100 °C include perchlorates, **41, 47, 51,** and **53.** However, the ΔT_m may result from differing degrees of hydrogen bonding between the cation and the perchlorate anion depending on the relative availability of the hydrogen atoms on the ring substituents.

Table 3. Structures and Thermal Properties of Quaternary Imidazolium Salts



Cpd	R	R'	R''	R'''	Y^-	$T_m (T_g)^a$	T_d^b	d_{calcd}^c
15	CH_3	H	CH_3	NO_2	ClO_4	172	259	1.72
16	CH_3	H	CH_3	NO_2	NO_3	163	174	1.59
17	CH_3	H	n-Pr	NO_2	ClO_4	148	260	1.59
18	CH_3	H	n-Pr	NO_2	NO_3	163	169	1.47
19	CH_3	H	n-Bu	NO_2	ClO_4	102	268	1.54
20	CH_3	H	n-Bu	NO_2	NO_3	95	158	1.42
21	CH_3	CH_3	CH_3	NO_2	ClO_4	186	307	1.65
22	CH_3	CH_3	CH_3	NO_2	NO_3	161	166	1.52
23	Et	CH_3	CH_3	NO_2	ClO_4	146	237	1.59
24	Et	CH_3	CH_3	NO_2	NO_3	65	146	1.47
25	CH_3	Et	CH_3	NO_2	ClO_4	168	291	1.59
26	CH_3	Et	CH_3	NO_2	NO_3	81	164	1.47
27	Et	Et	CH_3	NO_2	ClO_4	161	289	1.53
28	Et	Et	CH_3	NO_2	NO_3	127	188	1.42
29	CH_3	H	CH_3	H	NO_3	66	252	1.43
30	n-Pr	H	CH_3	H	ClO_4	(<-78°C)	307	1.48 (1.36^d)
31	n-Pr	H	CH_3	H	NO_3	(<-78°C)	289	1.33 (1.19^d)
32	n-Bu	H	CH_3	H	ClO_4	(<-78°C)	281	1.43 (1.31^d)
33	n-Bu	H	CH_3	H	NO_3	26	201	1.29 (1.18^d)
34	H	N_3	H	H	ClO_4	116	132	1.73
35	H	N_3	H	H	NO_3	124	124	1.89

[a] Melting point (T_m), °C; phase transition temperature (T_g), °C; [b] Thermal degradation, °C;

[c] Calculated density; [d] Measured density using a pycnometer, 25 °C, g/cm^3.

Scheme 4

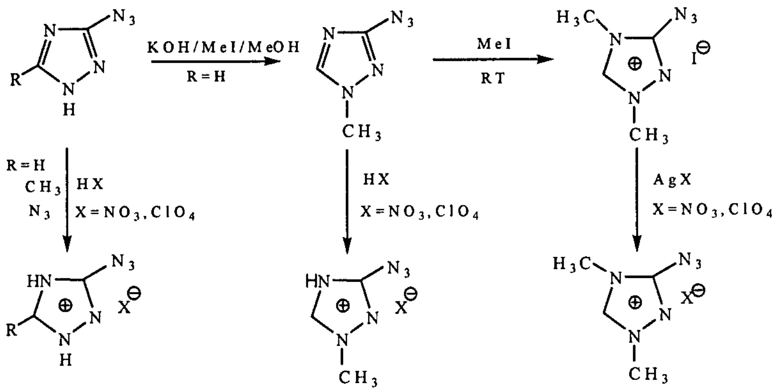
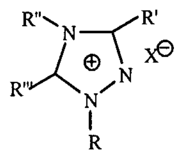


Table 4. Structures and Thermal Properties of Quaternary Triazolium Salts



Cpd	R	R'	R''	R'''	X^-	$T_m(T_g)$[a]	T_d[b]	d_{calcd}[c]	$\Delta_f H_m$[c,d]
36	CH_3	N_3	CH_3	H	NO_3	98	129	1.56(1.58[e])	-
37	CH_3	N_3	CH_3	H	ClO_4	68	147	1.69	-
38	H	N_3	H	H	NO_3	147	174	1.80 (1.79[e])	326.28
39	H	N_3	H	H	ClO_4	123	154	1.95	369.48
40	CH_3	N_3	H	H	NO_3	66	139	1.66	301.43
41	CH_3	N_3	H	H	ClO_4	55	147	1.80	353.19
41'	n-C_3H_7	N_3	H	H	ClO_4	(-65)	165	1.63[f]	-
41"	n-C_4H_9	N_3	H	H	ClO_4	(-55)	139	1.60[f]	-
42	H	N_3	H	CH_3	NO_3	118	136	1.68	230.93
43	H	N_3	H	N_3	NO_3	97	136	-	-
44	CH_3	H	CH_3	H	NO_3	1	160	-	-
45	CH_3	H	CH_3	H	ClO_4	(-34)	97	1.48[g]	-
46	NH_2	H	H	H	NO_3	121	149	1.75	72.84
47	NH_2	H	H	H	ClO_4	91	235	1.92	126.64
48	NH_2	H	CH_3	H	NO_3	(-62)	217	1.60(1.25[f]	45.67
49	NH_2	H	CH_3	H	ClO_4	108	253	1.77	91.32
50	H	H	NH_2	H	NO_3	69	181	1.75	77.06
51	H	H	NH_2	H	ClO_4	83	208	1.92	117.20
52	CH_3	H	NH_2	H	NO_3	(-60)	221	1.60 1.46[f])	57.62
53	CH_3	H	NH_2	H	ClO_4	86	259	1.77 (1.70[e])	106.94
53'	Et	H	NH_2	H	ClO_4	(-55)	167	1.58[g]	-
54	NH_2	H	H	NH_2	NO_3	159	183	1.76	-
55	NH_2	H	H	NH_2	ClO_4	138	217	1.93	-

[a] Melting point (T_m),°C; [b] Thermal degradation,°C; [c] Calculated density, g/cm^3; [d] Molar enthalpy of formation, kJ/mol; [e] From x-ray structure; [f] Measured density using a pycnometer, 25 °C, g/cm^3.

Single crystal X-ray structure determination of **36** which had been synthesized from 1-methyl-3-azido triazole by quaternization with methyl iodide clearly shows methyl substitution at N-4. A single crystal X-ray study was carried out on 3- azido-1, 2, 4-triazolium nitrate **(38)**. As expected, the proton is attached to N-4 of the 1, 2, 4-triazole ring. This is consistent with the quaternary results of 1-alkyl-1, 2, 4-triazoles with alkyl iodides. Examination of the crystal structure of **38** illustrates the influence of significant hydrogen bonding between the nitrate anion and the protonated 1, 2, 4-triazolium ring (Figures 1 and 2) which explains its rather high density of 1.79 g/cm^3 and melting point of 147 °C compared

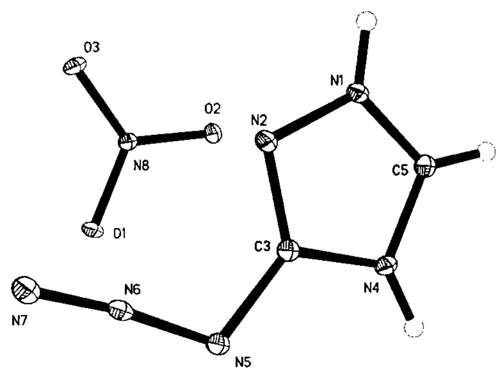


Figure 1. A thermal ellipsoid (30%) drawing of **38.**

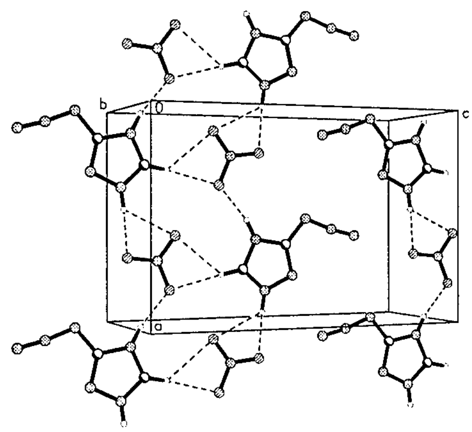


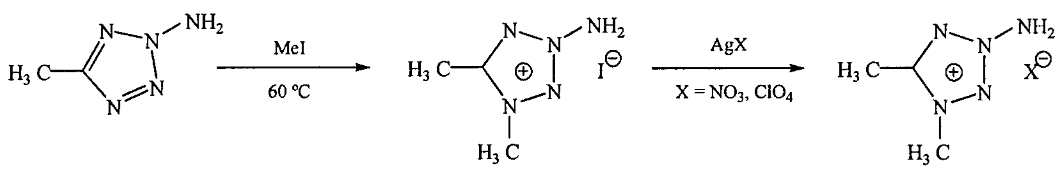
Figure 2. Ball and stick packing diagram of **38** showing the unit cell including hydrogen bonding.

to that of compound **(36)** (d = 1.58 g/cm^3) and melting point of 98 °C. The single crystal X-ray structure of **53** clearly shows the significant hydrogen bonding between the perchlorate anion and amino group, and that the methyl group is attached to N-1 of the 1, 2, 4-triazolium ring. This is consistent with Drake's results where 4-amino-1, 2, 4-triazole can be quaternized with nitric (or perchloric) acid since the N-amino group acts as an electron withdrawing group in high nitrogen heterocycles.

e. Syntheses and Thermal Properties of Quaternary Tetrazolium Salts.[19]

Tetrazolium perchlorate salts have higher melting points and decompose at higher temperatures than the nitrate derivatives. The densities of these salts range between 1.5 – 1.7 g/cm^3. All of the new tetrazolium salts have positive heats of formation ranging between 130 – 911 kJ/mol with the perchlorates being five or six times as positive as the analogous nitrates. 2-Amino-4, 5-dimethyl tetrazolium perchlorate (**61**) has a much higher melting point, T_d and ΔH_f than 1-amino-4, 5-dimethyltetrazolium perchlorate (**59**) [140 vs 51 °C; 238 vs 182 °C; 911 vs 539 kJ/mol] which may correlate somewhat with the extent of the hydrogen bonding. Perchlorates **57, 59, 61** have higher values than nitrates **56, 58, 60** for all properties studied – T_m, T_d, d, ΔH_f. One of the tetrazolium nitrates (**58**) melts < 25 °C and only three of the new salts (**58, 59, 60**) melt < 100 °C (Scheme 5, Table 5).

Scheme 5

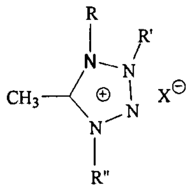


The solid state structure of **60**, which crystallizes in the chiral space group P2(1)2(1)2(1), (orthorhombic), shows that the N4 atom of the tetrazole was methylated. There is extensive, strong hydrogen bonding between the tetrazole cation and the nitrate group ranging from 2.857(2) to 3.295(3)Å (donor – acceptor). There is one bifurcated hydrogen bond between N8 and O1, O2(2.857(2), 2.944(2)Å) and O2 and O3 have three hydrogen bonds each. This synthon joins the ions together into a complicated 3D network (Figures 3 and 4).

f. Syntheses and Thermal Properties of Guandinium-Based Salts.[23]

While most of the 30 guanidinium-based ionic liquids synthesized show low melting points (< 100 °C), only 12 had melting points or phase transition temperatures < 25 °C (Scheme 6 - imidazolium and triazolium derivatives). Of the 12, six (**63, 67, 70, 71, 71, 74**) exhibit positive heats of formation (Table 6). Their thermal stabilities vary over a wide range, e. g., for the six liquids T_d = 272, 271, 265, 211, 284, 197 °C. The densities of these materials fall over a narrow range ~1.2-1.4 g/cm^3.

Table 5. Structures and Thermal Properties of Quaternary Tetrazolium Salts



Cpd	R	R'	R''	X^-	$T_m(T_g)^a$	T_d^b	d_{calcd}^c	$\Delta_f H_m^{\circ d}$
56	-	CH_3	CH_3	NO_3	94	193	-	-
57	-	CH_3	CH_3	ClO_4	133	315	1.61	74.03
58	NH_2	-	CH_3	NO_3	(-59)	170	1.55(1.27^e)	141.11
59	NH_2	-	CH_3	ClO_4	51	182	1.71	183.84
60	-	NH_2	CH_3	NO_3	94	173	1.55(1.53^f)	132.03
61	-	NH_2	CH_3	ClO_4	140	238	1.71	179.46

[a] Melting point (T_m), °C; phase transition temperature, °C; [b] Thermal degradation, °C; [c] Calculated density, g/cm^3; [d] Molar enthalpy of formation, kJ/mol; [e] Measured density using a pycnometer, 25 °C, g/cm^3; [f] From X-ray structure.

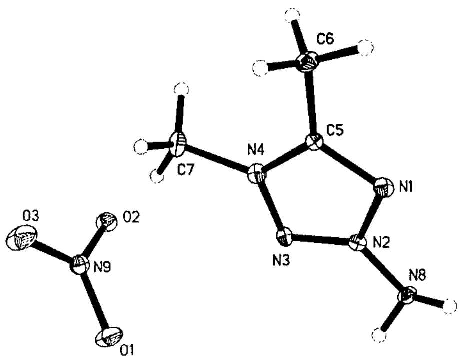


Figure 3. A thermal ellipsoid (30%) drawing of 4, 5-dimethyl-2-amino-tetrazolium nitrate **(60)**.

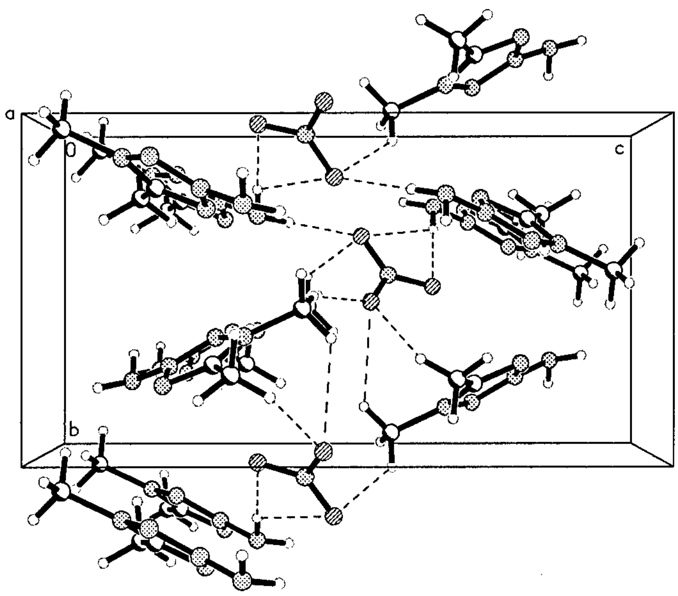


Figure 4. Unit cell of **(60)** showing hydrogen bonding between the tetrazolium cation and the nitrate anion.

Scheme 6

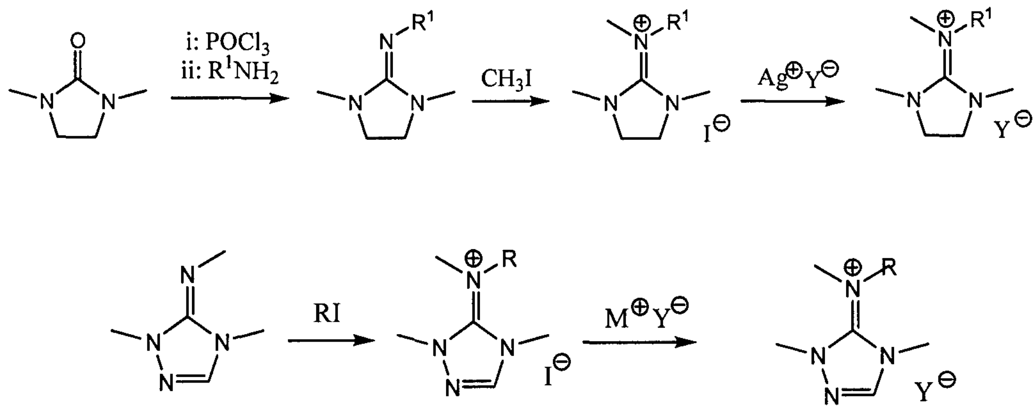
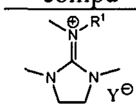
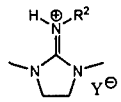
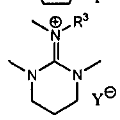
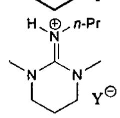
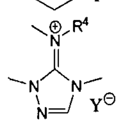


Table 6. Structures and Thermal Properties of Quaternary Guanidinium-Based Salts.

compd	Y	R	No.	Tm/Tg [a]	Td [b]	d_{calcd} [c]	$\Delta_f H_m$ [d]
	NO_3	*n*-Bu	**62**	7	246	1.20/1.23[e]	-274.3
		n-Pr	**63**	31	272	1.22	-259.9
	ClO_4	*n*-Bu	**64**	28	303	1.31/1.32[e]	-236.4
	NO_3	*n*-Pr	**65**	- [g]	128	1.26/1.24[e]	-270.2
		Me	**66**	3	130	1.32/1.34[e]	-237.6
	ClO_4	*n*-Pr	**67**	6	271	1.38/1.32[e]	-229.1
	NO_3	*n*-Bu	**68**	6	292	1.19/1.31[e]	-320.5
	NO_3		**69**	- [f]	127	1.24	-306.5
	ClO_4		**70**	-70[g]	265	1.35	-269.1
	NO_3	*n*-Bu	**71**	-69[g]	211	1.26	-268.1
	ClO_4	*n*-Bu	**72**	-59[g]	284	1.37	-231.5
		Me	**73**	125	276	1.49/1.53[h]	-180.9
	[i]	*n*-Bu	**74**	-66[g]	197		144.9

[a] °C. [b] °C. [c] g/cm³. [d] Molar enthalpy of formation; kJ/mol. [e] Measured density using a pycnometer at 25 °C. [f] Phase transition temperature < –78 °C. [g] Tg data. [h] From X-ray structure. [i] $N(NO_2)_2^-$.

Eleven of the salts contained perchlorate or nitrate as anion. Dinitroamide is the anion in **74.** Comparing the ΔH_f values for **71, 72** and **74** which differ only in the anion, NO_3^-, ClO_4^- and $N(NO_2)_2^-$, the positive numbers decrease ClO_4^- > $N(NO_2)_2^-$ > NO_3^-. The dinitramide salt has the lowest thermal stability followed by nitrate and than perchlorate (Table 6). Nearly all of the oxygen atoms of the perchlorate anion are involved in weak, nonclassical hydrogen bonding with the cations with donor-acceptor distances of 3.2-3.4 Å.

1, 4-Dimethyl-5-dimethylimino-1, 2, 4-triazolium perchlorate (**73**) crystallizes in the chiral orthorhombic space group P2(1)2(1)2(1). There are two independent ion pairs in the asymmetric unit and the solution inverted and overlain on the other, the weighted RMS deviation from fit is 0.0592 Å. The triazolium rings and the exocyclic NMe_2 groups are planar (Figures 5 and 6). This indicates that the lone pair on the exocyclic

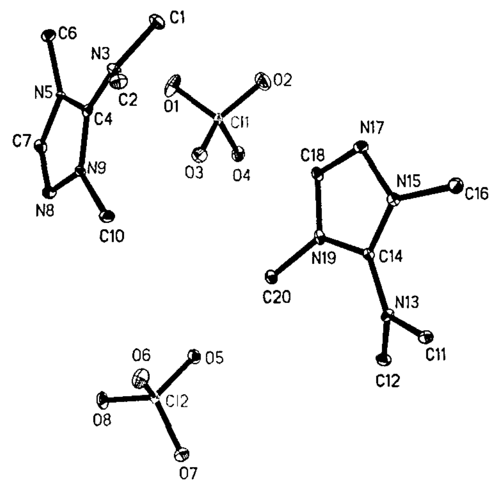


Figure 5. A thermal ellipsoid (30 %) drawing of **73**.

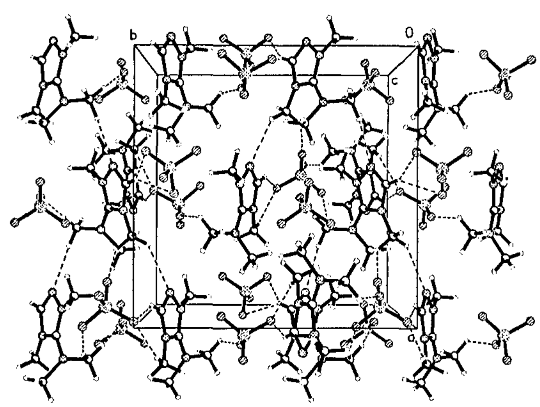


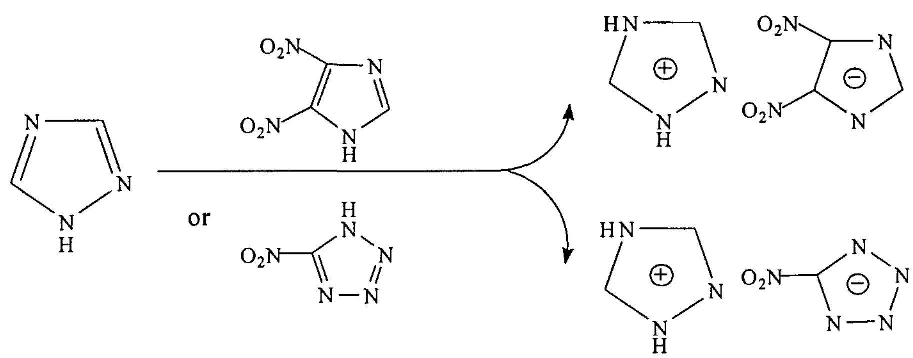
Figure 6. Packing diagram of **73** showing hydrogen bonding.

nitrogen atom is cross conjugated with the triazolium ring. This is also reflected in the bond lengths N3-C4 and N13-C14 which are considerably shorter than expected and are comparable to double bond distances. The extended conjugation can also be seen in the contraction of the endocyclic bonds in both cations. Sterically the NMe_2 group cannot become coplanar with the triazolium ring due to the dimethylation of the ring. Nearly all the oxygen atoms in the perchlorate anion are involved in weak non-classical hydrogen bonding with the cations with donor-acceptor distances of 3.2-3.4Å (Figure 6).

g. Syntheses and Thermal Properties of Energetic Azolium Azolate Salts.[26]

Five-membered nitrogen-containing heterocycles are traditional sources of energetic materials, and considerable attention is currently focused on azoles as energetic compounds, especially the 1, 2, 4-triazole series. Within the series of azoles, the relative energy characteristics (ΔH_f°) are dependent on the ring structures. We have synthesized several new ionic salts based on energetic azole type cations (2-azido-imidazolium and several substituted triazolium derivatives) and anions (4, 5-dinitro-imidazolate, 3-nitro-triazolate and 5-nitro-tetrazolate). Typical examples for preparation of such salts are given in Scheme 7. It has

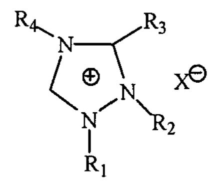
Scheme 7



been found that derivatives of 1, 2, 4-triazole were readily quaternized at N-4 with a concentrated strong acid (nitric or perchloric acid) in methanol. Both 4, 5-dinitro-imidazole and 5-nitro-tetrazole, with electron-withdrawing nitro-substituents on the ring, are strong NH acids ($pK_a = 0.8$ for 5-nitro-tetrazole). In this case, 4, 5-dinitro-imidazole and 5-nitro-tetrazole reacted to quaternize derivatives of variously substituted 1, 2, 4-triazoles at N-4 and also readily quaternized 2-azido-imidazole using methanol as solvent. The salts were formed in nearly quantitative yields and in high purity (**75, 76-81, 83-89**) (Table 7).

The single crystal X-ray structure determination of **84** clearly shows proton substitution at N-4 (N-13 in the structure). It also illustrates the influence of significant hydrogen bonding between the anion and the protonated 1, 2, 4-triazolium ring of **84** (Figure 7), forming hydrogen bonded ribbons. Due to the hydrogen bonding arrangement, i.e., each triazolium ring has a

Table 7. Structures and Thermal Properties of Substituted Azolium-Azolate Salts.



Compd	R_1	R_2	R_3	R_4	X	Tm(T_g) °C	T_d °C	d g/cm^3	ΔH_f kJ/mol
75[a]	-	-	-	-	NImi[b]	127	127	1.64	499.5
76	H	-	H	H	NImi	156	165	1.73	238.3
77	CH_3	-	H	H	NImi	102	150	1.66	206.8
78	H	-	N_3	H	NImi	92	158	1.70	599.7
79	CH_3	-	N_3	H	NImi	80	145	1.60	566.7
80	H	-	H	NH_2	NImi	137	149	1.65	354.9
81	-	NH_2	NH_2	H	NImi	153	165	1.64	294.9
82	H	-	H	NH_2	NTr[c]	64	198	1.50	839.9
83[a]	-	-	-	-	NTet[d]	112	137	1.51	697.9
84	H	-	H	H	NTet	137	183	1.53	436.3
85	CH_3	-	H	H	NTet	62	163	1.52	402.7
86	H	-	N_3	H	NTet	(-35)	161	1.53	800.9
87	CH_3	-	N_3	H	NTet	(-38)	141	1.45	768.5
88	C_3H_7	-	N_3	H	NTet	(-45)	153	1.40	719.4
89	H	-	H	NH_2	NTet	102	102	1.58	545.2

[a] Compounds 75 and 83 are 2-azido-imidazolium 4, 5-dinitro-imidazolate and 2-azido-imidazolium 5-nitro-tetrazolate, respectively. [b] 4, 5-Dinitro-imidazolate. [c] 3-Nitro-1, 2, 4-triazolate. [d] 5-Nitro-tetrazolate.

bifurcated C-H, a single C-H and a N-H hydrogen bond with each nitro-tetrazolate, a series of channels are formed along the a-axis, between the ribbons, as shown in the packing diagram (Figure 7). The channel dimensions are ca. 3 Å x 3.5 Å.

In Table 7, it is seen that the melting point of **85** (62 °C) is considerably lower than that of **84** (mp 137 °C). This likely occurs because a methyl group at N-1 in **85** has replaced a hydrogen atom in **84** reducing the possibility of hydrogen bonding between the anion and the

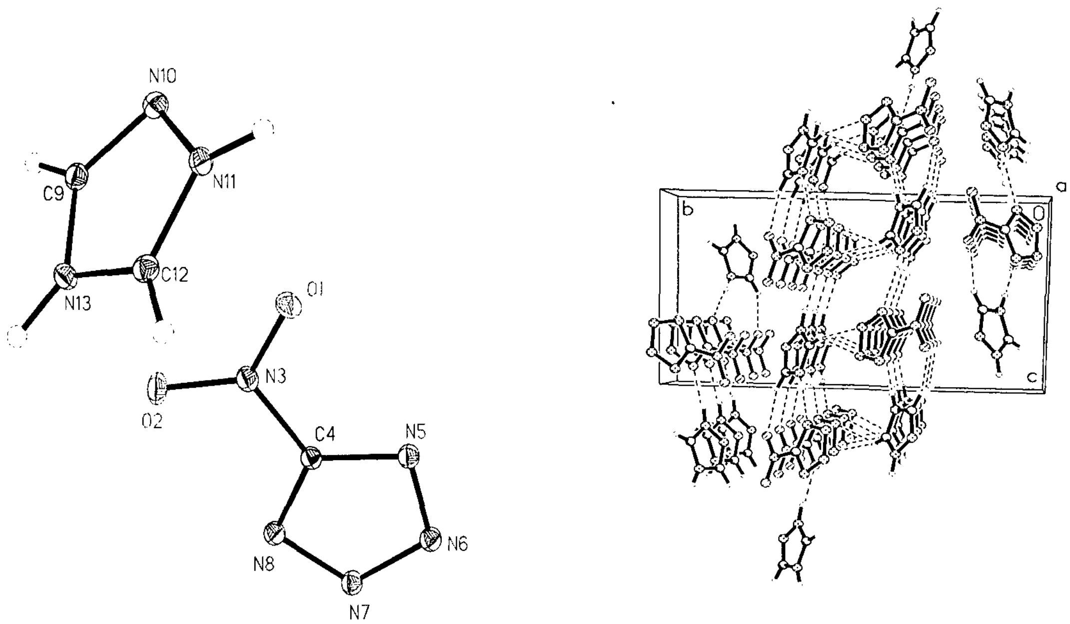


Figure 7. Thermal ellipsoid (30%) drawing of compound **84.** Unit cell of 1, 2, 4-triazolium 5-nitro-tetrazolate (**84**) showing hydrogen bonding (dashed lines) between anion and cation.

protonated 1, 2, 4-triazolium ring. 4-Amino-1, 2, 4-triazole also can react with 3-nitro-1, 2, 4-triazole in CH_3CN to form 4-amino-1, 2, 4- triazolium 3-nitro-1, 2, 4-triazolate (**82**) in high yield. Compounds with 5-nitro tetrazolate as the anion have lower melting points and higher molar enthalpies of formation than those of the analogous 4, 5-dinitro-imidazolate. Most of these new salts exhibit good physical properties, including relatively high densities (> 1.40 g/cm^3) and high positive heats of formation. In fact, all of these new compounds exhibit a positive heat of formation with **87** being the highest at 1070 kJ/mol.

h. Syntheses and Thermal Properties of 3, 5-Dinitro-1, 2, 4-triazolates.[19, 31]

In this work, we have prepared substituted 1, 2, 4-triazolium and tetrazolium salts with a common anion, 3, 5-dinitro-1, 2, 4-triazolate, in order to compare properties of interest, i. e., density, melting point and heat of formation, when the cation is varied. Through the use of the

Scheme 8

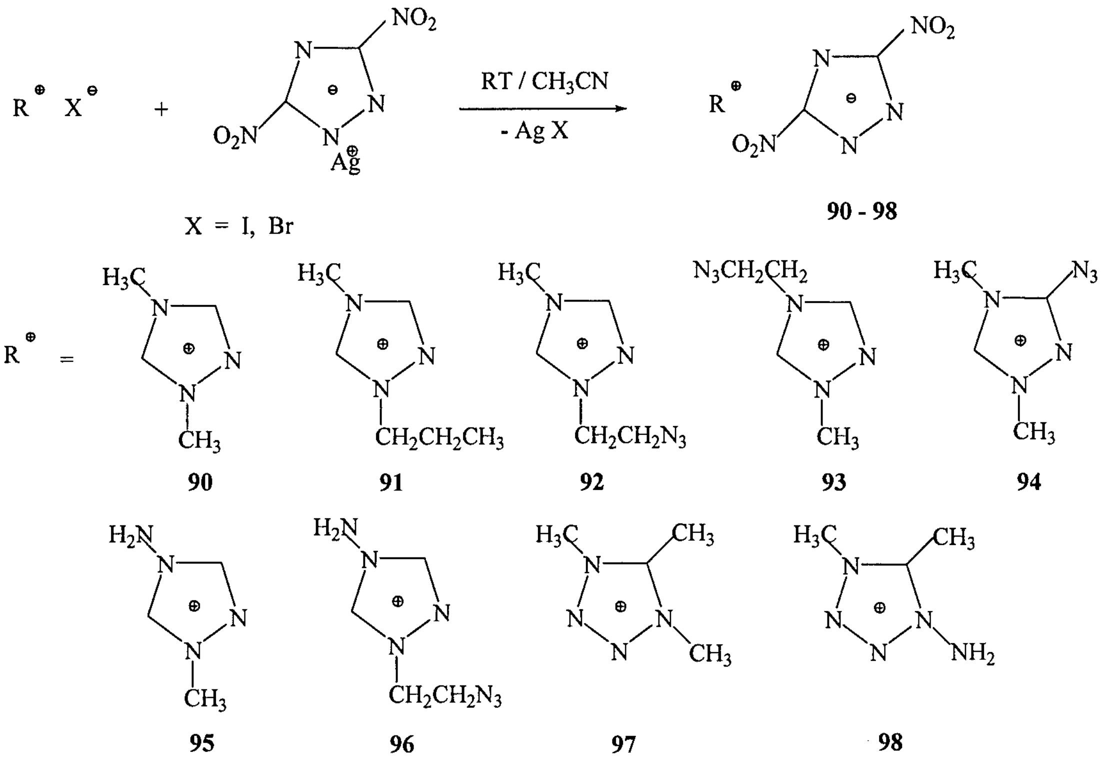


Table 8. Properties of azolium 3, 5-dinitro-1, 2, 4-triazolates

Compd	Y	R^1	R^2	R^3	R^4	T_m (T_g) °C	T_d °C	d g cm^{-3}	ΔH_f kJ/mol
90	C	CH_3	-	H	CH_3	97	239	1.86	230.7
91	C	$CH_3CH_2CH_2$	-	H	CH_3	61	231	1.51	200.3
92	C	$N_3CH_2CH_2$	-	H	CH_3	88	189	1.61	582.2
93	C	CH_3	-	H	$N_3CH_2CH_2$	-43 (T_g)	179	1.71[g]	580.7
94	C	CH_3	-	N_3	CH_3	-22 (T_g)	118	1.60[g]	598.6
95	C	CH_3	-	H	NH_2	112	234	1.70	382.6
96	C	$N_3CH_2CH_2$	-	H	NH_2	126	204	1.65	700.0
97	N	-	CH_3	CH_3	CH_3	173	199	1.72	317.5
98	N	-	NH_2	CH_3	CH_3	141	166	1.64	462.4
99[a]	C	CH_3	-	H	NH_2	-60(T_g)	221	1.55	
100[b]	C	CH_3	-	H	NH_2	86	259	1.66	
101[a]	N	-	NH_2	CH_3	CH_3	-59(T_g)	170	1.50	
102[b]	N	-	NH_2	CH_3	CH_3	51	182	1.71	

[a] NO_3^-, [b] ClO_4^-

silver 3, 5-dinitro-1, 2, 4-triazolate, metathetical reactions giving products in nearly quantitative yields and high purity were possible in acetonitrile (Scheme 8, Table 8). The single crystal X-ray structure of **98** is shown in Figure 8. There are two independent ion pairs in the asymmetric unit

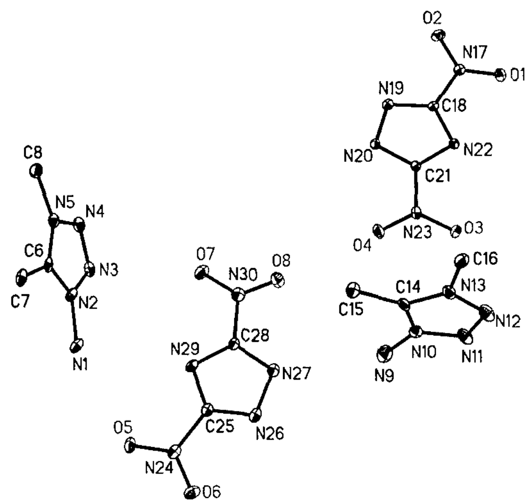
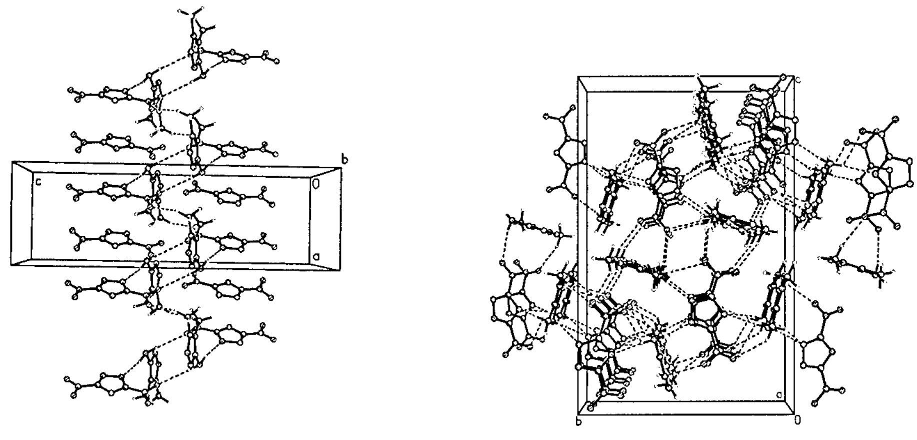


Figure 8. Thermal ellipsoid (30%) plot of **98** showing both independent cation/anion pairs. Hydrogen atoms have been omitted for clarity.

with significant hydrogen bonding between the 4, 5-dimethyl-1-aminotetrazolium cation and 3, 5-dinitro-1, 2, 4-triazolate anion. Hydrogen bonding is based between the NH_2 groups and the anions and ranges from N-H...O (3.07-3.43Å) and N-H...N (3.09-3.24Å) and forms large 14 atom rings. There are also some weak C-H...O hydrogen bonds between C15-H15c...O8, (3.50Å), which link the double cation/anion hydrogen bonded ring systems into spirals which run parallel to the a-axis (Figure 9a). These spirals are joined together via a complex array of hydrogen bonding to form a 3D network (Figure 9b).

Comparison of the melting points of compounds **90**, **91** and **92** (Table 8), illustrates clearly the influence of the cation, e. g., the melting point for compound **91** (mp 61 °C), which has a propyl group at N-1 of the 1, 2, 4-triazolium ring, is considerably lower than that of methyl group at N-1 of the 1, 2, 4-triazolium ring in **2** (mp 97 °C). The melting point for **92** (mp 88 °C),



(a) **(b)**

Figure 9. (a) Ball and stick image of the spiral arrangement parallel to the a-axis; (b) 3D network of hydrogen bonding between spiral units – compound **98.**

which has the 2-azidoethyl group at N-1 of the triazolium ring falls between those of **90** and **91**. It can be seen, by comparison of the melting points and decomposition temperatures of **92** and **93,** that the influence of the position of the substituted group on the triazolium ring also plays an important role, e. g., the melting point for **92** is 88 °C, and decomposition occurs at 189 °C; for **93**; melting occurs at -43 °C (T_g) and decomposition at 179 °C (T_d), respectively. 1, 4-Dimethyl-3-azido-1, 2, 4-triazolium 3, 5-dinitro-1, 2, 4-triazolate (**94**) (T_g -22 °C) is also liquid at room temperature. For 4-amino-1, 2, 4-triazolium derivatives (**95, 96**) and tetrazolium derivatives (**97, 98**), the melting points are higher than 100 °C.

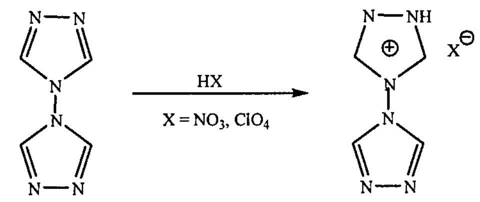
By comparison of compounds **90, 91** and **92,** it can seen that the impact of different substituted groups at N-1 of 1, 2, 4-triazolium on heats of formation of corresponding salts, which varies as 1-(2-azidoethyl)-1, 2, 4-triazolium > 1-propyl-1, 2, 4-triazolium > 1-methyl-1, 2, 4-triazolium (+395.2, +198.7, and +118.1 kJ mol^{-1}), respectively. The marked influence of the position of the substituent on the triazolium ring is easily observed by comparing ΔH_f values between compounds **92** and **93**, at +395.2 and +771.3 kJ mol^{-1}, respectively. For compounds **90**

(ΔH_f +118.1 kJ mol^{-1}) and **94** (ΔH_f +778.1 kJ mol^{-1}), the enhancement achieved by the presence of the azido group on the triazolium ring is clearly demostrated.

In addition, by comparing the thermal properties of compounds **95, 99** and **100,** or **98, 101** and **102,** it can be seen that for the same triazolium or tetrazolium cation, the heats of formation of compounds with 3, 5-dinitro-1, 2, 4-triazolate as anion, are considerably higher than those of corresponding compounds with perchlorate or nitrate as anion, e.g., ΔH_f for compounds **98**, **101** and **102** are +660.3, +129.5 and +538.5 kJ mol^{-1}, respectively.

i. **Quaternary Salts containing Bi-triazoles.**[29]

4, 4'-Bi(1, 2, 4-triazole) was synthesized according to the literature from 4-amino-1, 2, 4-triazole and N, N-dimethylformamide azine using p-toluenesulfonic acid as catalyst It was readily quaternized with one equivalent of nitric or perchloric acid in a solution of methanol and acetonitrile (1/1, v/v) as solvent to form the expected ionic salts **103** and **104,** in nearly quantitative yields and in high purity (Scheme 9). They melt at 150 and 187 °C, respectively. The structure of **103** was confirmed by single crystal X-ray analysis (Figure 10). Compound **103** crystallizes in the monoclinic space group P2(1)/c with four molecules in the asymmetric unit. The compound consists of two crystallographically independent ions, 1H-4, 4'-bi(1, 2, 4-triazolium) as well as the nitrate group. The two triazole rings are almost perpendicular to each other, with a dihedral angle of 92.4°. The linking N-N distances between the rings is 1.383(1)Å. One of the most notable features about this compound is the closeness and orientation of the nitrate anion to the organic cation. The nitrate group lies above the protonated triazolium ring and is canted at an angle of 58.4° to this ring. The O1-N11-O3 vector is somewhat aligned to the C7-C10 vector in the ring with short contacts between the cation and anion at O2...C7, 3.183Å and O1...C10, 2.790 Å. The O1-N11-O3 moiety of the nitrate group forms the same type of arrangement with the nearest symmetry generated organic cation. In this case the nitrate is canted at 82.0° to the plane of the triazole ring with slightly longer anion-cation distances; O1...N3, Scheme 9



103 (X = NO_3), 104 (X = ClO_4)

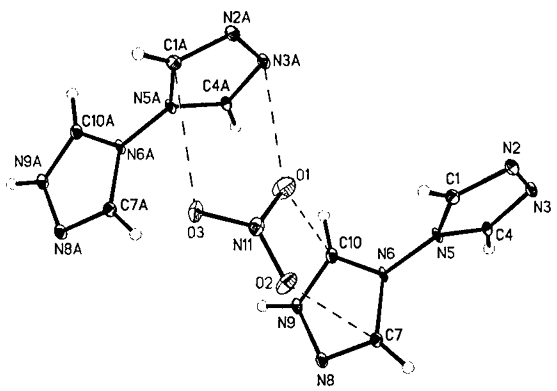
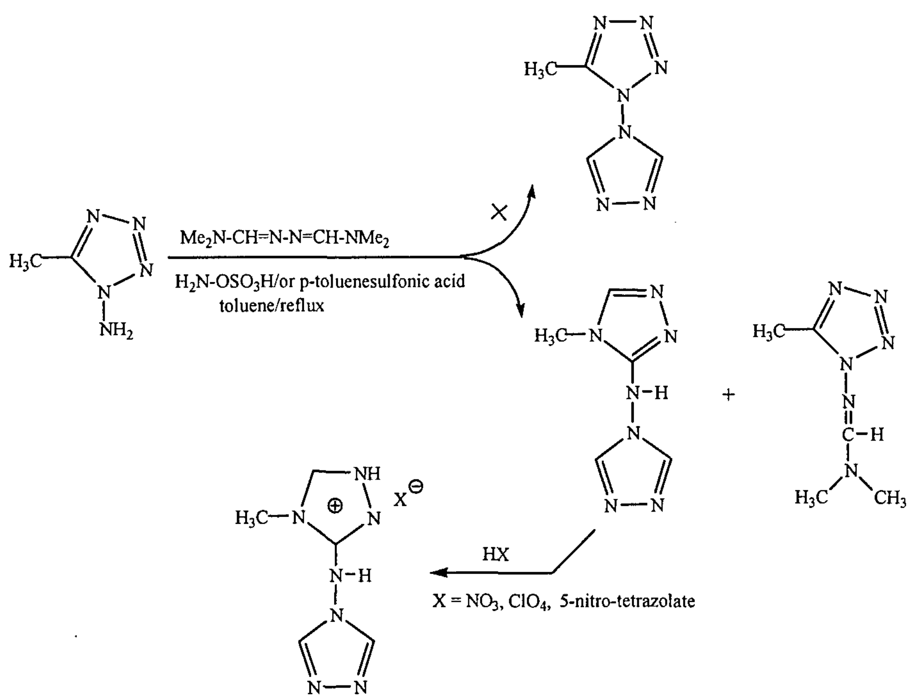


Figure 10. The plot (**103**) showing the relative orientation of the NO_3 group to the cation. Dashed lines indicate close approaches. A second symmetry generated (1+x, y, z) cation is also shows its orientation relative to the NO_3 group. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms are shown but are not labeled.

3.004 Å and O3...C1, 3.308 Å. The shortest hydrogen bond is formed between the protonated nitrogen and next nearest nonprotonated ring N9...$N3^i$ 2.693(1) Å (i = x+1, -y+3/2, z+1/2 symmetry transformation). There are a variety of weak non-classical hydrogen bonds to the nitrate group, ranging from 2.95 – 3.33 Å, which extend the system into a three dimensional aggregate.

In order to introduce tetrazole derivatives into N, N-linked biazoles, 1-amino-5-methyltetrazole and N, N-dimethylformamide azine were reacted using reaction conditions identical to those for the formation of 4, 4'-bi(1, 2, 4-triazole). However, the N, N'-linked target product 4-(5-methyl-tetrazole)-1, 2, 4-triazole was not obtained. Rather, N-4-(1, 2, 4-triazole)-N-3-(4-methyl-1, 2, 4-triazole) amine was formed in low yield (5 %), and the main product was N, N-dimethyl-N'-(5-methyl-tetrazole)methanimidamide (Scheme 10). When H_2NOSO_3H was used as catalyst, the yield of the amine was increased to 38 %.

Scheme 10



105, 106, 107

The amine can be protonated with one equivalent of nitric or perchloric acid or 5-nitro-tetrazole in methanol as solvent to form salts **105, 106** and **107** in high yield. Single crystal X-ray structure determination of **106** clearly illustrates the influence of significant hydrogen bonding between the perchlorate anion and the protonated 1, 2, 4-triazolium ring (Figure 11). From the packing diagram, the structure is composed of inorganic perchlorate layers along the *bc* plane which sandwich the organic bi-triazolium cations and water molecules. There is extensive hydrogen bonding within the organic/water layer, with the water molecule forming both donor and acceptor short hydrogen bonds to three different bitriazolium cations.(O5...N10, N11, 2.82,

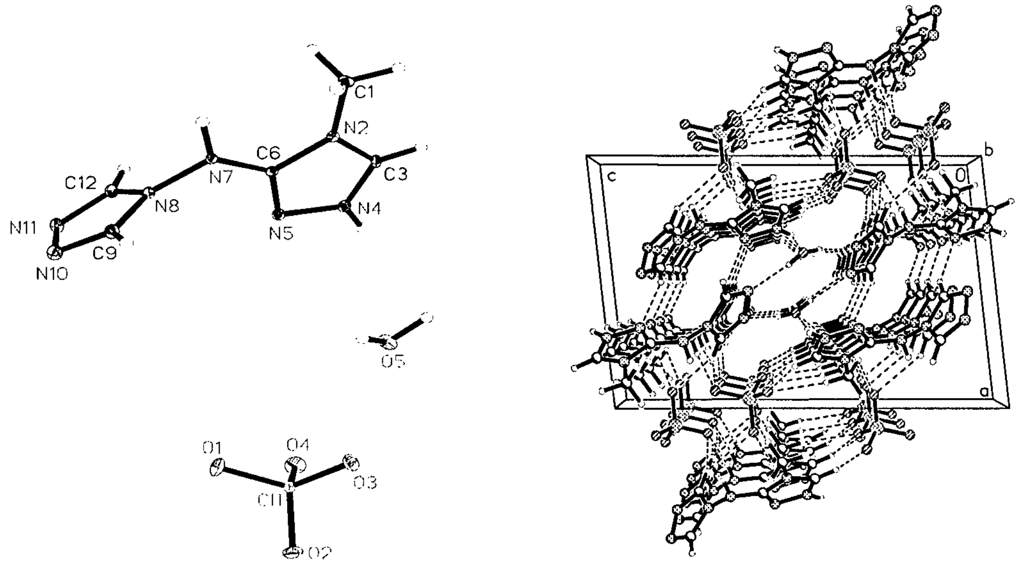


Figure 11. (a) Thermal ellipsoid plot (30%) of **106**. Hydrogen atoms are not labeled. (b)Packing diagram of **10** showing extensive hydrogen bonding (dashed lines).

2,88 Å; N4...O5, 2.63 Å). Each bi-triazolium cation forms one weak hydrogen bond with the adjacent bi-triazolium cation (C9...N5, 3.23 Å) resulting in a twisted four unit chain parallel to the *b*-axis. These are linked in turn by the water molecules forming the extended organic layer. There are multiple hydrogen bonds to each perchlorate anion ranging from 2.83-3.31 Å. These tie the whole assembly together in an extended 3 D array. The multiplicity of strong hydrogen bonding supports the high density of 1.85 g/cm^3 and melting point of 239 °C.

Derivatives of substituted triazoles were readily protonated with 5-nitro-tetrazole, which is a strong NH acid (pK_a for 5-nitro-tetrazole is – 0.8), to form corresponding ionic salts in high yields.[26] In this case, compound **107** was obtained from the amine and 5-nitro-tetrazole (Scheme 10). The melting point is 143 °C.

Densities and the standard enthalpies of formation are important properties of energetic salts. It can be seen from Table 9 that the densities for compounds with perchlorate as anion are

Table 9. Physical Properties and Heats of Formation for Bis(1, 2, 4-triazolium) and 1, 2, 4-triazole-4-methyl-1, 2, 4-triazolium Amine Salts

Compd	T_m °C	T_d °C	d g/cm^3	ΔH_f kJ/mol
103	150	150	1.73	849.7
104	187	235	1.83	913.0
105	102	102	1.64	773.4
106	239	265	1.85	842.8
107	143	163	1.45	1256.3

higher than that of the analogous nitrate, e.g., the densities of the nitrate salt **105** and perchlorate salt **106** are 1.64 and 1.85 g/cm^3, respectively. Typical experimental results of constant volume combustion energies and calculated standard molar enthalpies of combustion and standard molar enthalpies of formation (ΔH_f) were obtained using a literature method which was previously employed for similar salts. These values are included in Table 9. Comparing the standard molar enthalpies of formation (ΔH_f) of **103** and **104**, and **105** and **106**, it is seen that when perchlorate is the anion, the standard molar enthalpy of formation of **104** or **106** is higher than those of corresponding compounds of nitrate as anion (**103** or **105**). The standard molar enthalpies of formation for **103** and **104** are higher than those of **105** and **106**. When 5- nitro-tetrazolate was the anion, the resulting compound, **107,** had the highest standard molar enthalpy of formation, 508.0 kJ/mol (1814.4 kJ/kg) of the compounds described.

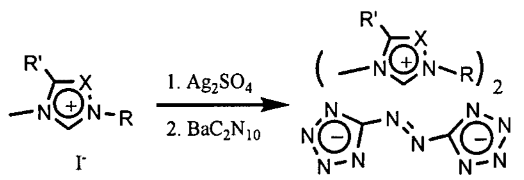
N-4-(1, 2, 4-triazole)-N-3-(4-methyl-1, 2, 4-triazole)amine and its salts were obtained and their molar enthalpies of formation were lower than those of the N, N-linked bi(1, 2, 4-triazolium) salts. The melting points, thermal degradation temperatures and the standard heats of formation for compounds with perchlorate as anion are higher than those of the analogous nitrates, while the highest heats of formation were obtained when 5-nitro-tetrazolate was used as the energetic anion.

j. Energetic Salts Which Contain Azotetrazolate (AT), Iminobis(5-tetrazolate) (IBT) and 5, 5'-Bis(tetrazolate) (BT) Anions.[25]

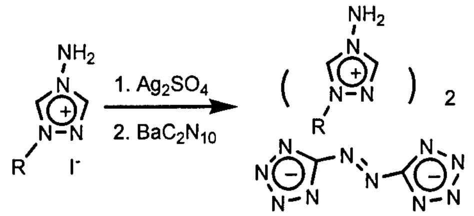
Sodium and barium 5,5'-azotetrazolates were used as starting materials and were synthesized according to the literature. Initially, an effort was made to metathesize triazolium nitrate or sulfate directly with barium 5,5'-azotetrazolate, but decomposition of the azotetrazolate anion to give nitrogen gas occurred due to its instability in the presence of acid. However, the use of quaternized imidazolium iodide salts followed by two metathetical reaction steps readily gave the desired azotetrazolate. Thus, compound **108** (Scheme 11) was readily prepared, which was an ionic liquid at room temperature melting at 3 °C similar to 1-butyl-3-methylimidium 3,5-dinitrotriazolate. This is unprecedented since most of the known azotetrazolates are solid with melting points higher than 160 °C. However, the heat of formation for compound **108** is -2,273 kJ kg^{-1}. (Tab;e 10) For comparison, 1-methyl-4-nitroimidazole was quaternized with methyl iodide at 90 °C, followed by a metathesis reaction resulting in salt **109** which exhibits a heat of formation of +2,999 kJ kg^{-1}. The latter is higher than that of **TAG-AT**. Encouraged by this result, we prepared some substituted triazolium and azido-triazolium azotetrazolate salts.

4-Amino-1, 2, 4-triazole itself has a rather high calculated heat of formation at +318 kJ/mol. Although its azotetrazolate salts have lower nitrogen content than **TAG-AT**, its two quaternized salts, **112** and **113**, exhibit very high heats of formation, at +4,360 kJ kg^{-1} and +4,679 kJ kg^{-1}, respectively. The structure of **112** is further supported by X-ray single crystal structuring. The hydrogen atoms on N7 were disordered over the mirror plane. Interestingly, the unit cell packs as a layered structure with hydrogen bonds with the distance between the two layers at 3.04 Å and as shown in Figure 12 , there are hydrogen bonds between the cation and anion, and the hydrogen atom on C(12) participates in two hydrogen bonds.

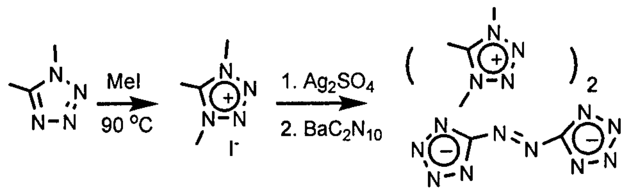
Scheme 11



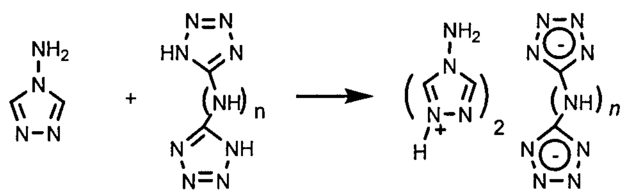
108 : X = C, R = n-butyl, R' = H; **109**: X = C, R = Me, R' = NO_2;
110: X = N, R = Me, R' = H; **111**: X = N, R = Me; R' = N_3



112: R = CH_3; **113**: R = NH_2



114



115: n = 1; **116**: n = 0

A trimethyltetrazolium salt was also obtained by quaternization of 1, 5-dimethyltetrazole with methyl iodide at 90 °C. Frequently the quaternized products of 1, 5-disubstituted tetrazoles give rise to two isomers, but in this case, under higher reaction temperature, only the 1, 2, 5-

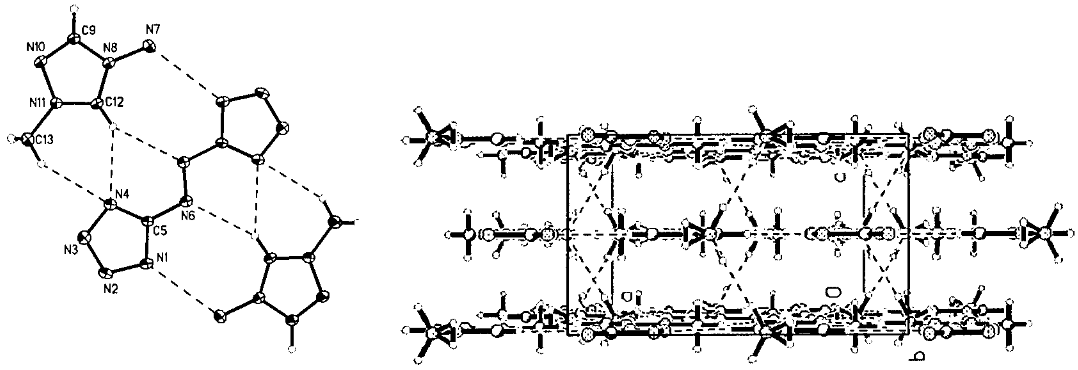


Figure 12. Thermal ellipsoid (30%) plot of **112**. Only unique atoms are labeled. Disordered hydrogen atoms have been removed for clarity (upper) and a packing diagram (down).

quaternized azotetrazolate salt, **114**, was obtained. This was found to have a relatively low positive heat of formation, +1547 kJ kg^{-1}. Although there are several reports of the salts of iminobis(5-tetrazolate) (**IBT**) and 5,5'-bis(tetrazolate) (**BT**), most of them are described in patents or unpublished documents, and there is a paucity of data available for comparison. Therefore, we prepared the salts of **IBT** and **BT**. In refluxing methanol, they can readily quaternize 4-amino-1, 2, 4-triazole to give the corresponding energetic salts **115, 116**. With regard to the heats of formation of the salts of these three dianions, **BT** ranks lower than **AT** but much higher than **IBT**. Interestingly, in sharp contrast, the **BT** salt has a much lower melting point.

Density is an important physical property of any new energetic material. As shown in Table 10, the densities of the most salts range from 1.5 to 1.6. Noteworthy, with the exception of compound **114,** none of azotetrazolate salts contains water of hydration or solvent as determined by NMR and elemental analysis. Decomposition of azotetrazolates salts **108-114** occurs violently at the melting point. In contrast to **AT** salts, the **IBT** salt, **115,** evolved gas gently at its melting point, and the **BT** salt, **116,** is stable at its melting point at 131 °C, but decomposes violently at 182 °C by DSC. Most of the salts are stable for storage at room temperature for two months except for **113,** which spontaneously evolves N_2 gas.

Table 10. Properties of AT, IBT and BT energetic salts.

Compd.	T_m °C	Density g cm^{-3}	ΔH_f kJ/mol
108	3	1.26	906
109	145	1.54	1108
110	182	1.42	1139
111	155	1.55	1856
112	180	1.57	1364
113	- [a]	1.59	1613
114	189	1.46	1301
115	175	1.59	1256
116	131	1.61	1183

[a] melting point not observed, decomposes violently at 134 °C.

In conclusion, ionic salts of **AT** and **BT** exhibit high heats of formation compared to **IBT** salt, and **IBT** salt show markedly different thermal behaviors from **AT** and **BT** on microwave heating.

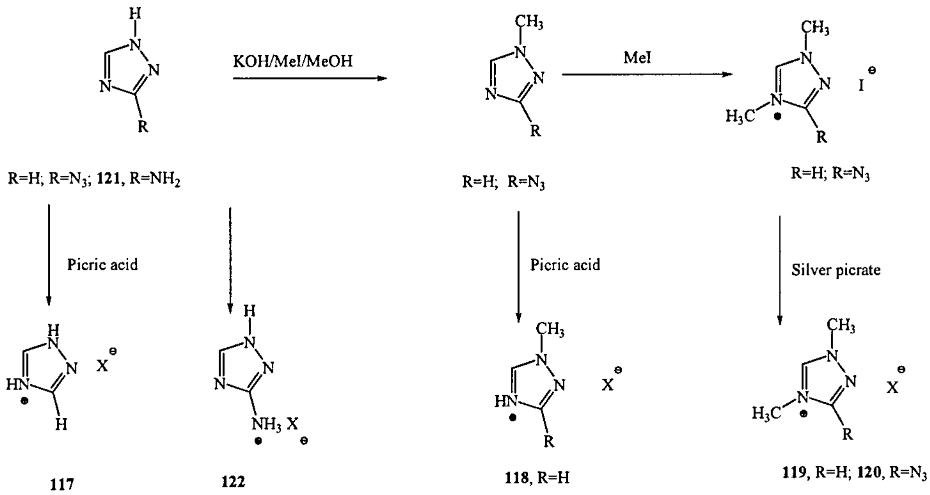
k. Syntheses of Mono and Bridged Azolium Picrates as Energetic Salts.[30]

The enthalpy criteria of energetic chemical systems are governed by their molecular structures. In moving from imidazole ($\Delta H_f°_{(cryst)}$ = 58.5 kJ/mol) to 1, 2, 4-triazole ($\Delta H_f°_{(cryst)}$ = 109 kJ/mol) to tetrazole ($\Delta H_f°_{(cryst)}$ = 237.2 kJ/mol), the variation in the trend of the heats of formation is increasingly positive. High nitrogen compounds containing polyazides possess even more positive heats of formation because their energy content rapidly increases with the number of energetic azido groups in the molecule. However, they tend to be extremely sensitive to spark, friction, and impact as well as to heat. We have reported new energetic salts obtained by the quaternization of azido or nitro derivatives of imidazole, 1, 2, 4-triazole and substituted derivatives of tetrazole with nitric or perchloric acid or with iodomethane followed by metathesis reaction with silver nitrate or silver perchlorate.[22] While these compounds with azide-containing triazolium cations (nitrate or perchlorate anion) do exhibit marginally high positive heats of formation, recently reported molecular azides of triazine are considerably more energetic with considerably higher heats of formation, e. g., 2, 4, 6-triazido-1, 3, 5- triazine (+1053 kJ/mol) and 4, 4', 6, 6'-tetra(azido)azo-1, 3, 5-triazine (+2171 kJ/mol).

Now, we have studied salts with energetic mono and bridged azolium cations with picrate as the anion, and have determined their physical and thermodynamic properties. Additionally, these properties have been compared, in some cases, with their analogues where the anion is nitrate or perchlorate. The presence of the picrate anion(s) combines an oxygen-rich anion with a high nitrogen azolium cation thus providing the opportunity for high positive heats of formation. Although anhydrous picric acid tends to be unstable, and its impact and friction sensitivities are higher than that of TNT, many organic and inorganic picrate salts have been created and studied; however, none consists of diazolium cations combined with picrate.

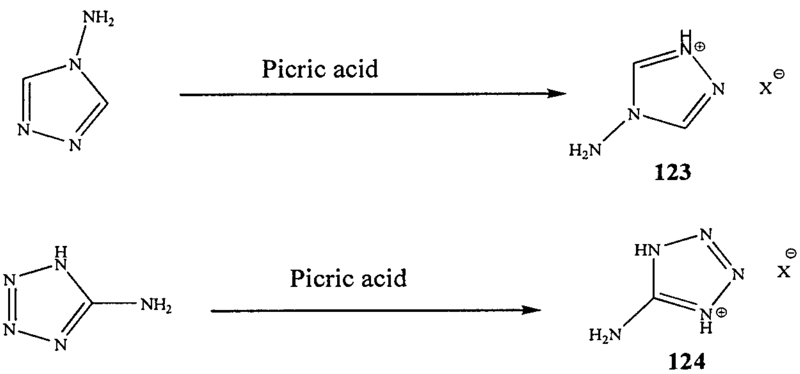
Triazolium or substituted triazolium picrates were prepared either via direct reaction with picric acid in methanol (**117, 118**) or metathesis with silver picrate after quaternization of the parent triazole with methyl iodide (**119, 120**) (Scheme 12). The triazolium iodides were prepared based on the literature. Although earlier we were able to quaternize azido-substituted triazoles with concentrated nitric or perchloric acid,[22] the analogous reactions of the azides with picric acid failed under a variety of conditions. This likely arises from the lower acidity of picric acid (pKa = 0.3) compared to nitric acid (pKa = -1.44) and with the concomitant decrease in the basicity of the triazolium ring because of the presence of the azide group. However, 1, 4-dimethyl-3-azido-1, 2, 4-triazolium picrate (**120**) can be readily obtained from the azide when metathesized with silver picrate (Scheme 12). Quaternization of 3-amino-1, 2, 4- triazole (**121**) did not occur at the N-4 position in the triazolium ring, but rather compound **122** resulted from the ready protonation of the 3-amino group. This same phenomenon was observed when concentrated nitric or perchloric acid was used, that is, a substituted ammonium salt ($RNH_3^+X^-$, $X = NO_3^-$, ClO_4^-) was formed analogous to **122.**

Scheme 12



However, 4-amino-1, 2, 4-triazole was readily quaternized with picric acid in methanol by protonating the ring at N-1 to give the triazolium salt **123** in high yield (Scheme 13). This is supported by single crystal X-ray structure showing quaterniazation at N-1 (Figure 13).

Scheme 13



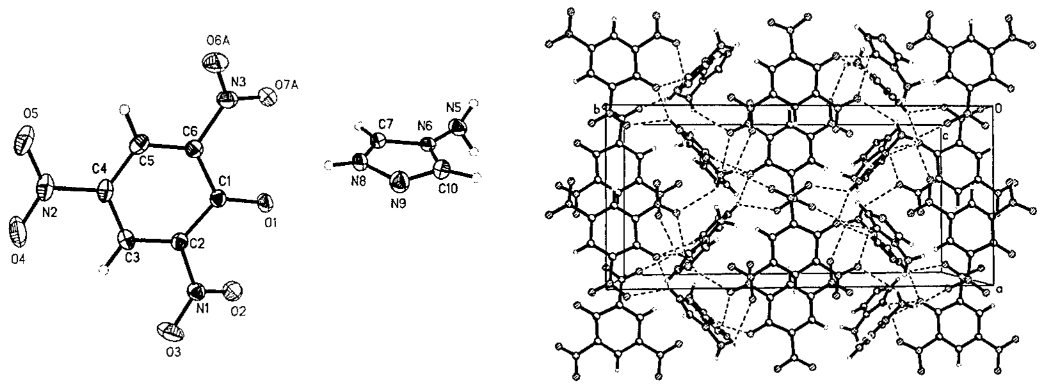


Figure 13. (a) 30% probability thermal ellipsoid plot of **123**. Only one conformation for the disordered NO_2 group is shown. Hydrogen atoms are shown but are unlabelled for clarity. (b) A packing diagram of **123** Dashed lines indicate hydrogen bonding. Zig-zag sheets of triazolium cations tie the rows of picrates into a crosslinked 3D array.

Surprisingly, quaternization of 5-amino-tetrazole (C-amino group) (Scheme 12) occurs at the N-4 position in the tetrazolium ring in high yield, and not at the amino group at C-5, to form the salt, 5-amino-1, 2, 4-tetrazolium picrate, **124**. The single crystal X-ray structure, **124**, is given in Figure 14.

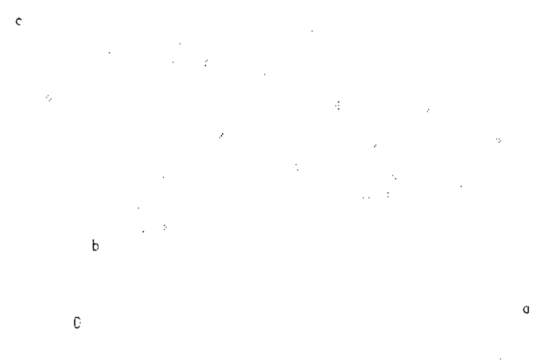
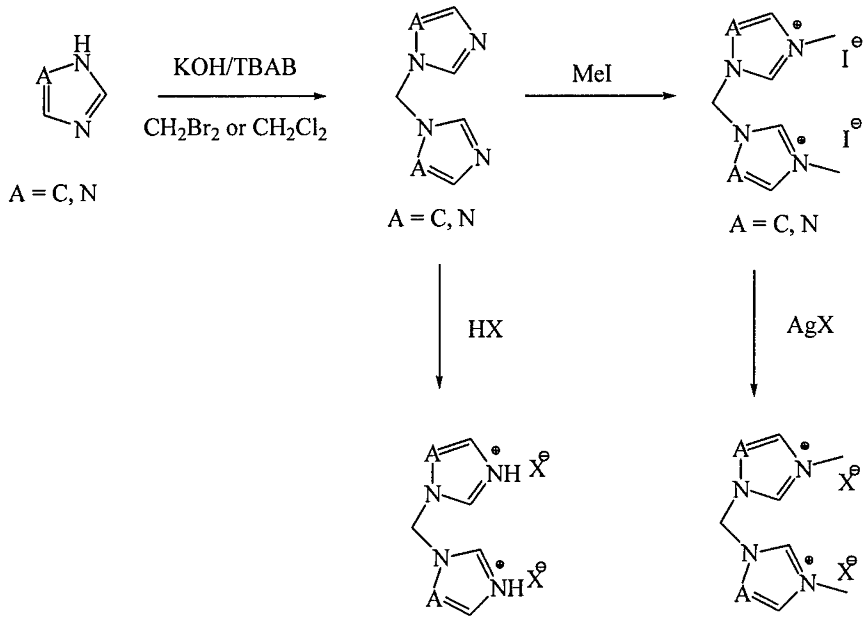


Figure 14. (a) 30% probability thermal ellipsoid plot of **124**. Hydrogen atoms are shown but are unlabelled for clarity. (b) A packing diagram of **124**. Only one sheet section is shown. Hydrogen bonding is indicated by dashed lines.

There is a paucity of energetic salts with bridged cations. In order to examine the physical and thermodynamic properties of mono and diazolium salts containing a common anion, bridged bis(imidazolium) or bis(triazolium) methane compounds were obtained from the reaction of imidazole or triazole with dibromo or dichloromethane under basic conditions and in the presence of a phase transfer catalyst (Scheme 14).[27]

Scheme 14



125 A = C, X = picrate
126 A = N, X = nitrate

127 A = C, X= picrate
128 A = N, X= picrate
129 A = N, X= nitrate

These bridged azolium species were either 1) reacted with picric or nitric acid to form the picrate, **125**, or nitrate, **126;** however, the bridged tetrazolium species did not react with picric acid to give the corresponding dipicrate; or 2) quaternized with methyl iodide to the respective iodides which were subsequently metathesized with silver picrate or nitrate forming **127, 128** and **129.** Each of the picrate or nitrate salts was isolated in a yield >88%. Compound **129** is readily soluble in water, but **125-128** are not miscible with water. In general, all of these new picrate and nitrate salts are hydrolytically stable (Table 11).

Table 11. Phase Transition and Decomposition Temperatures, Densities and Thermochemical Results of Picrates, Nitrates and Perchlorates

			Picrate			Nitrate		Perchlorate	
Cpd	T_m [a]	d [b]	OB [d]	T_d [e]	$\Delta_f H^\circ_m$ [f]	T_d [e]	$\Delta_f H^\circ_m$ [f]	T_d [e]	$\Delta_f H^\circ_m$ [f]
117	169	1.77	-67	196	265.2	182	-	285	-
118	91	1.72	-79	185	228.2				
119	141	1.80	-91	271	195.7	160	-	97	-
120	106	1.48	-78	176	563.3	129	-	147	-
122	235	1.60	-66	244		HMS			
123	197	1.64 [c]	-66	228	381.2	181	-109.7	208	298
124	147	1.85 [c]	-53	214	406.8				
125	215	1.52	-36	283	249.5				
126	153	1.54	-46		-218.4	188	177.3		
127	184	1.63	-93	313	159.8				
128	216	1.67	-81	242	369.5				
129	-15(T_g)		-74			162	-195.7		
TAG-AT		1.60	-73		1075				
HMX		1.91	-21		75				
TNT		1.65	-74		-64				
Picric acid		1.77	-43		-213.6				
RDX		-	-22		83.8				

[a] Melting point (T_m) (°C) / phase transition temperature (T_g) (°C), [b] Measured density using pycnometer (g/cm^3), [c] Density from crystal structure for **123** is 1.72 and **124** is 1.84, [d] OB (%) is oxygen balance which was calculated from OB = 1600[(a + b/2 –d)/ FW] for a compound with the molecular formula of $C_aH_bN_cO_d$, [e] Thermal degradation temperature (T_d) (°C), [f] Molar enthalpy of formation (kJ/mol

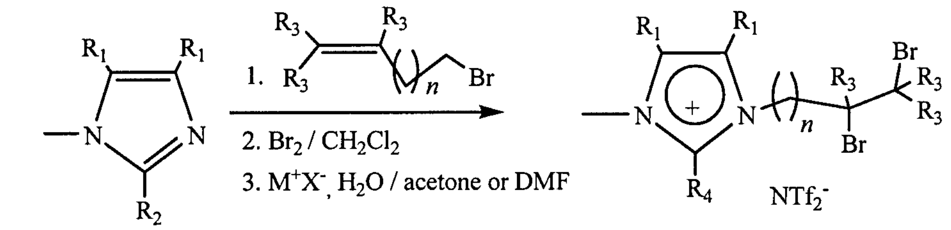
In general the bridged azolium picrates are somewhat more stable thermally than their monocationic picrate analogues as shown by their decomposition temperatures, e. g., **128**, T_d = 242 °C, is higher than **118**, T_d =185 °C. Also, the picrates are more thermally stable than nitrates or perchlorates, e. g., 4-amino-1, 2, 4-triazolium picrate (**123**) decomposes at 228 °C compared with the nitrate and perchlorate which decompose at 181 °C and 208 °C, respectively.

Mono and bridged azolium picrate and nitrate salts were synthesized and their physical and thermochemical properties compared. The thermal stabilities of the salts are dipicrates> picrates > perchlorates > nitrates while the densities are found to average ~1.60 g/cm^3. Although it is not possible to quaternize 3-C-amino triazole, the 4-amino triazole easily reacted at N-1. In contrast, the 5-amino tetrazole (C-5) was readily quaternized at N-4. Their structures were confirmed by single crystal X-ray analysis. The heats of formation values for picrates are more positive than for analogous nitrates and perchlorates. Oxygen balance values for the mono and bridged azolium picrates and dipicrates fall in the range of many common energetic materials.

l. Synthesis of Very Dense Halogenated Liquids.[15]

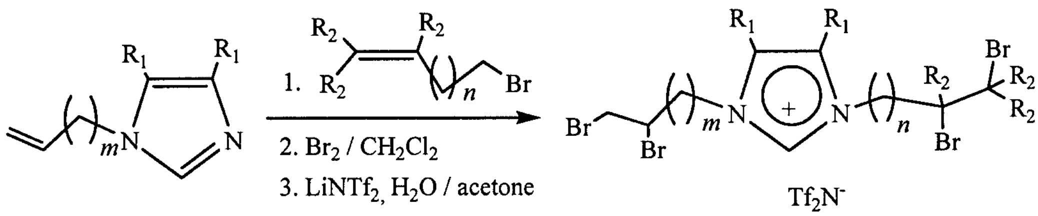
While these highly halogenated, thermally and hydrolytically stable ionic liquids are not energetic compounds, because of their high densities, they are of considerable interest for possible use as damping/-flotation fluids. In order to obtain a melting or phase transition point below 25 °C, bis(trifluoromethanesulfonyl)amide is the anion (Scheme 15). With densities ranging from 1.95 to 2.80 g/cm^3, these stable materials, which are readily prepared by a one-pot procedure, fall at the high end of the usual dense liquids such as 1, 1, 3, 5, 5-pentabromoper-fluoropentane (~2.62 g/cm^3) and 1, 1, 3, 5, 7, 7-hexabromo-perfluoroheptane (~2.65 g/cm^3) (Table 12).

Scheme 15



130 $n = 1$, $R_1 = R_2 = R_3 = R_4 = H$ **132** $n = 1$, $R_1 = R_2 = Br$, $R_3 = R_4 = H$

131 $n = 2$, $R_1 = R_2 = R_4 = H$, $R_3 = F$ **133** $n = 1$, $R_1 = I$, $R_2 = R_3 = R_4 = H$



134 $m = 1$, $n = 1$, $R_1 = R_2 = H$ **136** $m = 1$, $n = 2$, $R_1 = H$, $R_2 = F$

135 $m = 0$, $n = 1$, $R_1 = R_2 = H$ **137** $m = 1$, $n = 1$, $R_1 = I$, $R_2 = H$

Table 12. Yields, Physical Properties for Halogenated Ionic Liquids

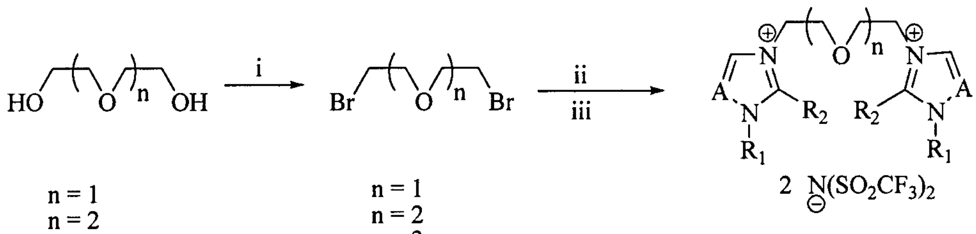
Compound	Yield / %	Tg (Tm)[a] /°C	Td[a] /°C	Density[b] / g cm^{-3}
130	90	-52	268	1.95
131	75	-55	284	2.11
132	85	-24	307	2.26
133	70	-16	287	2.55
134	86	-34	250	2.22
135	84	-24	246	2.25
136	69	-32	273	2.35
137	68	-2.9	282	2.80

[a]Tg, Td, DSC, [b]density, pycnometer

m. Polyethylene Glycol Functionalized Dicationic Ionic Liquids with Alkyl or Polyfluoroalkyl Substituents as High Temperature Lubricants.[36]

A series of new polyethylene glycol functionalized dicationic ionic liquids with alkyl or polyfluoroalkyl substitutents (**138 – 146** and **147 – 152**) has been prepared (Schemes 16 and 17).

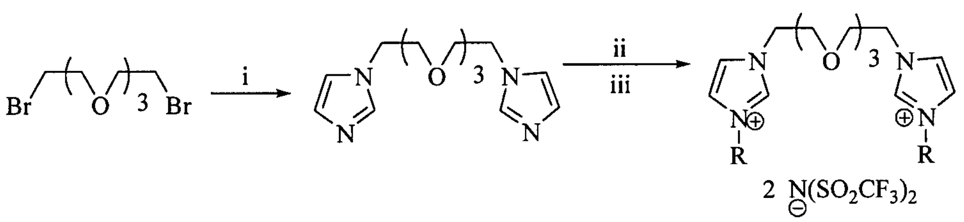
Scheme 16



138 - 141 n = 1-4, $R_1 = CH_3$, R_2 = H, A = C
142 n = 3, $R_1 = R_2 = CH_3$, A = C
143 -146 n = 1-4, R_1 = butyl, R_2 = H, A = N

Reagents and conditions: i) PBr_3/ether, reflux, 12h; ii) alkylimidazole, 80°C, 16h or 1-butyltriazole, 110°C, 20h; iii) $LiN(SO_2CF_3)_2$, CH_3OH+H_2O = 10:1, R.T. 2h.

Scheme 17



147, R = $CH_2CH_2CH_3$
148, R = $CH_2CH_2CF_3$
149, R = $CH_2(CH_2)_2CH_3$
150, R = $CH_2(CH_2)_2CF_3$
151, R = C_6H_{13}
152, R = $CH_2CH_2C_4F_9$

Reagents and conditions: i) imidazole, NaH, THF, 70°C, 24h; ii) RBr or RI, 80°C or 110°C, 20h; iii) $LiN(SO_2CF_3)_2$, $CH_3OH + H_2O$ = 10:1, R.T. 2h.

Important physical properties of these liquids, including glass transition (T_g) and decomposition temperatures (T_d), solubility in common solvents, density (d) and viscosity (η) were measured.

These ionic liquids show high thermal stability and good lubricity. In general, imidazolium based dicationic liquids have higher T_d (> 415°C) than their triazolium analogues. The introduction of polyfluoroalkyl groups boosts antiwear properties but also leads to a decrease in T_d. These ionic liquids also exhibit excellent tribological characteristics even at 300°C, which suggests use as high temperature lubricants (Table 13).

Ionic liquids (**138-146, 147-152**) were characterized by their ^{1}H, ^{13}C and ^{19}F NMR spectra, and elemental analyses. The solubilities of the dicationic ionic liquids with NTf_2^- anions were determined at room temperature. In general, they are immiscible with hexane, diethyl ether, water and miscible with methanol, acetone and ethyl acetate. The thermal properties of these dicationic ionic liquids were determined by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The fundamental properties including density (d) and dynamic viscosity (η) at different temperatures (30°C and 60°C) are presented in Table 1. All of these new ionic liquids have low glass transition temperatures (T_g) in the range of -32°C to -64°C. The length of the linkage polyether chains separating the geminal dications (ranging from one ether to four ether chains) and the nature of the dication (imidazolium **138 – 142** versus triazolium **143 – 146**) appear not to influence their glass transition temperatures, e. g., **138 – 142** with T_g = -47 °C to -52 °C and **143 – 146** with T_g = -43 °C to -54 °C. These results are slightly different than the observations described in the literature, where the length of alkyl chain links were found to affect the melting points of the various geminal dicationic ionic liquids. In our case where the anion is invariably NTf_2^-, an anion whose negative charge is dispersed over its entirety, the cation-anion interactions are reduced resulting in lower glass transition temperatures of approximately the same value (Table 13).

In order to determine the tribological properties, four compounds were chosen for Optimol SRV (Schwingungs-Reibverschleiss-Pruefgeraet) tribology testing. As indicated, the ionic liquid with more polyether units (**146** vs **143**) shows better antiwear properties under low load, while resulting in high wear under high load (>500 Newtons). The result clearly confirms that the presence of fluorine (**150** vs. **149**) in the ionic liquid favorably boosts its anti-wear performance (Table 14).

Table 13. Physical and Thermal Properties of Geminal Dicationic Ionic Liquids 138 - 146 and 147 – 152.

Compd[a]	$[NTf_2^-]$	T_g (°C)[b]	T_d (°C)[c]	Density[d]	Viscosity[e]	
					30 °C	60 °C
138	$[CH_3O_1IM]$	-49	420	1.64	-	207
139	$[CH_3O_2IM]$	-52	430	1.62	562	92
140	$[CH_3O_3IM]$	-47	426	1.53	854	135
141	$[CH_3O_4IM]$	-52	429	1.52	705	119
142	$[2CH_3O_3IM]$	-56	457	1.55	409	80
143	$[C_4H_9O_1TA]$	-43	362	1.51	-	219
144	$[C_4H_9O_2TA]$	-54	365	1.48	554	102
145	$[C_4H_9O_3TA]$	-48	352	1.48	618	104
146	$[C_4H_9O_4TA]$	-48	348	1.47	727	97
147	$[C_3H_7O_3IM]$	-40	427	1.60	512	95
148	$[C_3F_3O_3IM]$	-32	388	1.68	1539	192
149	$[C_4H_9O_3IM]$	-62	438	1.47	459	91
150	$[C_4F_3O_3IM]$	-34	393	1.60	-	243
151	$[C_6H_{13}O_3IM]$	-64	415	1.43	327	71
152	$[C_6F_9O_3IM]$	-37	386	1.71	-	298

[a] For convenience, special notations were used. For example, $[CH_3O_1IM]$ represents ionic liquid (**138**) with one ether linkage chain (O_1), imidazolium cation (IM) and methyl group at 3-position of the imidazolium ring; while $[C_4H_9O_1TA]$ represents ionic liquid (**143**) with one ether linkage chain (O_1) triazolium cation (TA) and a butyl group at the 1-position of the triazolium ring. [b]Glass transition temperature. [c] Decomposition temperature. [d] g/cm^3 at 25 °C. [e]Determined by drop-ball method (η, cP)

In addition, two thermally stable ionic liquids (**142, 147**) were used as candidates for a temperature ramp test, where pure ionic liquids were put onto the surface of a steel vs. steel contact (M50 steel) and the temperature increased every 5000 cycles. The friction for ionic liquid

142 at 25 °C is very consistent, and an increase to 100 °C causes a slight reduction due to a decrease in viscosity. At 200°C the continuing decrease in viscosity will cause increasing

Table 14. SRV anti-wear properties of selected ionic liquids.

Compd.	Worn Volume ($x10^{-4}$ cm^3) under different load (N)				
	200	300	400	500	600
143	6.8	15.5	19.0	17.5	21.5
146	5.8	7.7	10.6	19.4	22.5
149	8.4	10.0	12.0	14.0	15.5
150	6.2	6.0	9.0	9.0	8.0

asperity contact and possibly the first signs of reaction which leads to the increased friction. At >300 °C, the surface reaction between the steel and the ionic liquid causes the friction to increase dramatically. Ionic liquid **147** was demonstrated to be much better than **142** and other most common ionic liquids by lasting and performing well through the 300°C tests. This result indicates that during operation at elevated temperatures, this ionic liquid can form thin, durable and stable surface boundary layers that maintain low friction and wear (Figure 15).

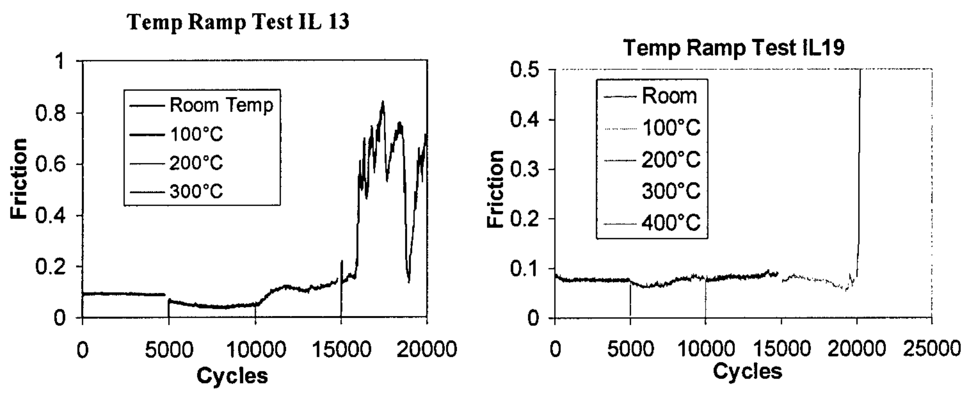


Figure 15. Temperature-ramp friction testing results for **142** and **147.**

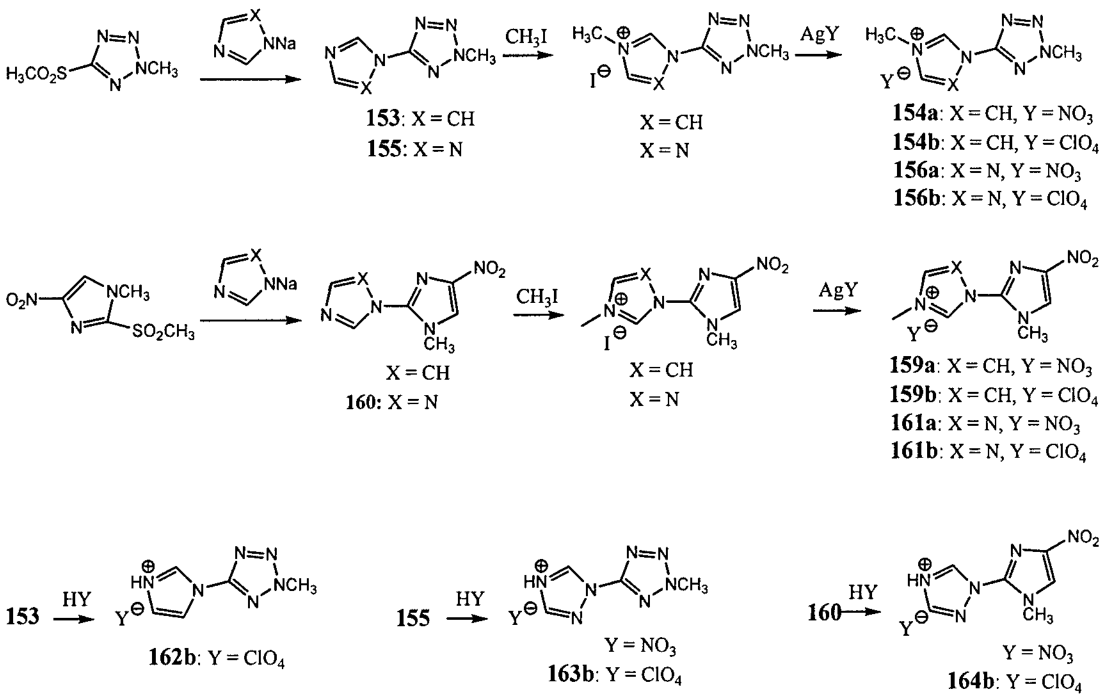
n. Energetic Bicyclic Azolium Salts.[41]

In order to determine the energies associated with compounds that contain two linked azole or azolium rings and to compare them with the bridged bicyclic azolium salts, we prepared several nitrate and perchlorate salts with linked identical as well as different five-membered nitrogen heterocycles. In the past, preparation of N-C-bicyclic azoles or bicyclic azolium salts was accomplished frequently by using precursor rings substituted with a halogen, nitro or methylsulfonyl moiety as the leaving group. Replacement of halogen often required high temperature. When the nitro group was replaced, the composition and the ratio of reaction products were a function of the pK_a of the azole. In this work, we have prepared methylsulfonyl-substituted imidazole, triazole and tetrazole species, followed by reaction with sodium imidazolate or sodium triazolate under mild conditions to obtain a series of N-C-biazoles.

The bicyclic azoles were obtained from sodium imidazolate or sodium 1,2,4-triazolate in reaction with methylsulfonyl-substituted azoles, e. g., 1-methyl-5-(methylsulfonyl)-1*H*-tetrazole, 2-methyl-5-(methylsulfonyl)-2*H*-tetrazole and 1-methyl-2-(methylsulfonyl)-5-nitro-1*H*-imidazole. Bicyclic azoles when quaternized with methyl iodide produced iodide salts were further metathesized with silver nitrate or silver perchlorate to give energetic salts, **154, 156, 157, 158, 159, 161**. Bicyclic azoles, **153, 155, 160,** when reacted with nitric or perchloric acid, yielded salts, **162, 163, 164** (Scheme 18).

Phase transition temperatures (midpoints of melting points, Tm) for all the salts were determined by differential scanning calorimetry (DSC) as given in Table 15. With a common cation, the nitrates with the exception of **156** invariably had lower melting points than the perchlorates. The decomposition temperatures of the perchlorates ranged from 255 °C to 295 °C (except **158b** at 240 °C, **163b** at 229 °C and **164b** at 175 °C), while for nitrates the range was from 145 °C for **161a** to 190 °C for **159a,** invariably lower than perchlorates. Density and enthalpy of formation are important characteristics of energetic compounds and are governed by their molecular structures. Increasing the number of nitrogen atoms in a heterocycle results in a considerable gain in the heat of formation. The measured (calculated) densities of the nitrate and perchlorate salts fall between 1.519 (1.531) g/cm^3 for **154a** to 1.674 (1.784)g/cm^3 for **164b**. The densities which were calculated for the single crystal structures of **12b** and **21b** are also listed in Table 15. The calculated and experimentally determined densities agree reasonably

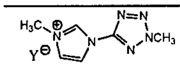
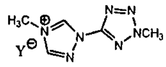
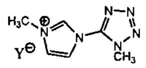
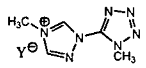
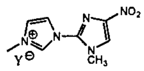
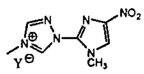
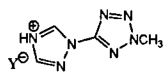
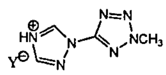
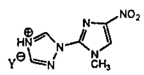
Scheme 18



closely to within – 0.4 % to 7.6 %. The calculated values for **158b** and **164b** and that obtained from single crystal structure calculations agree within 1.0 % and 0.4 % respectively. The calculated results for enthalpies of formation are also given in Table 15. They range from 209.9 to 412.3 kJ mol^{-1}; all are higher than the values of TNT, HMX, and TATB

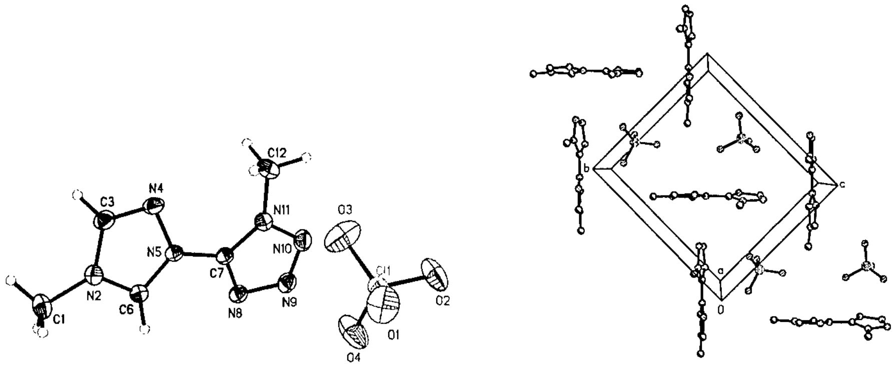
Solid state structures were obtained for **158b** and **164b**. Data for both structures were obtained at 185 K due to crystal instabilities at lower temperatures. The asymmetric unit for each ion pair, **158b** and **164b**, are shown in Figures 16 and 17. There are relatively few heterobicyclic

Table 15. The structures and properties of bicyclic azolium salts.

comp	Y	No	T_m[a] (°C)	T_d[b] (°C)	d_{calcd}[c] (g/cm^3)	d_{meas}[d] (g/cm^3)	$\Delta_f H_{Lattice}$[e] (kJ/mol)	$\Delta_f H_m$[f] (kJ/mol)
	NO_3	**154a**	79	175	1.531	1.519	--	--
	ClO_4	**154b**	110	283	1.653	1.631	--	--
	NO_3	**156a**	151	151	1.574	1.515	489.1	310.8
	ClO_4	**156b**	141	293	1.695	1.639	472.2	357.7
	ClO_4	**157b**	159	295	1.653	1.648	--	--
	ClO_4	**158b**	152	240	1.695	1.645/ 1.678[g]	475.0	426.5
	NO_3	**159a**	125	190	1.574	1.581	--	--
	ClO_4	**159b**	169	289	1.678	1.641	--	--
	NO_3	**161a**	-	145	1.612	1.566	--	--
	ClO_4	**161b**	227	282	1.716	1.652	--	--
	ClO_4	**162b**	150	255	1.725	1.623	--	--
	NO_3	**163a**	154	166	1.644	1.565	493.2	341.8
	ClO_4	**163b**	128	229	1.773	1.648	479.5	385.5
	NO_3	**164a**	153	165	1.676	1.617	474.4	209.9
	ClO_4	**164b**	-	175	1.784	1.674/ 1.767[g]	468.7	245.6
TNT[h]								-64
HMX[i]								75
TATB[j]								-154

[a] Melting point; [b] Thermal degradation; [c] Calculated density, g/cm^3; [d] Measured density using gas pycnometer at 25 °C. g/cm^3; [e] Molar lattice energy, calcd.; [f] Molar enthalpy of formation, calcd.; [g] From X-ray structure; [h] 2, 4, 6-trinitrotoluene; [i] octahydro-1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazocine; [j] 1, 3, 5-triamino-2, 4, 6-trinitrobenzene.

(i.e., triazole-imidazole, triazole-triazole or triazole-tetrazole) systems in the literature and due to protonation and differences in substitution no direct comparisons can be made.



a b

Figure 16. a) A thermal ellipsoid (30%) drawing of **158b**. b) ball and stick packing diagram of one layer in **158b** viewed down the a axis, showing the alternating perpendicular cation motif held together by weak hydrogen bonding.

The 3D packing of **158b** and **164b** are quite different. In **158b**, an alternating perpendicular cation layer motif is seen (Fig. 16b). This is held together with weak hydrogen bonding between the cation and the perchlorate oxygen atoms (3.1-3.4 Å, 138-151 °). There is also weak hydrogen bonding between the cations (C1...N9^{i}, 3.449(3) Å,

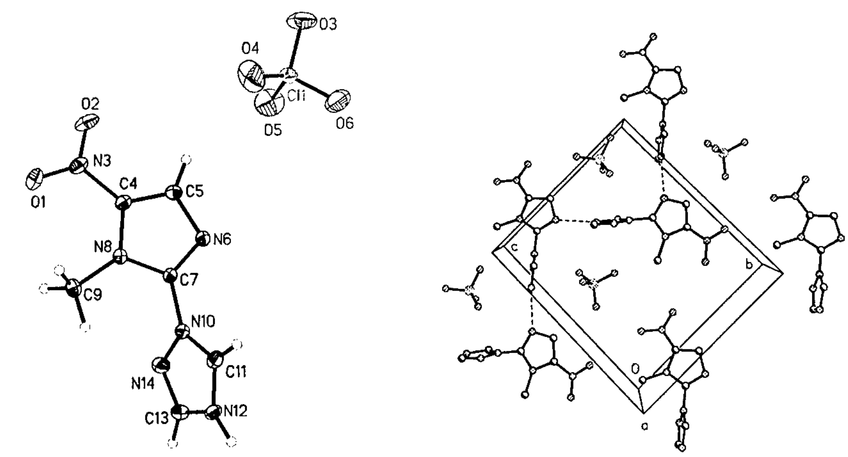


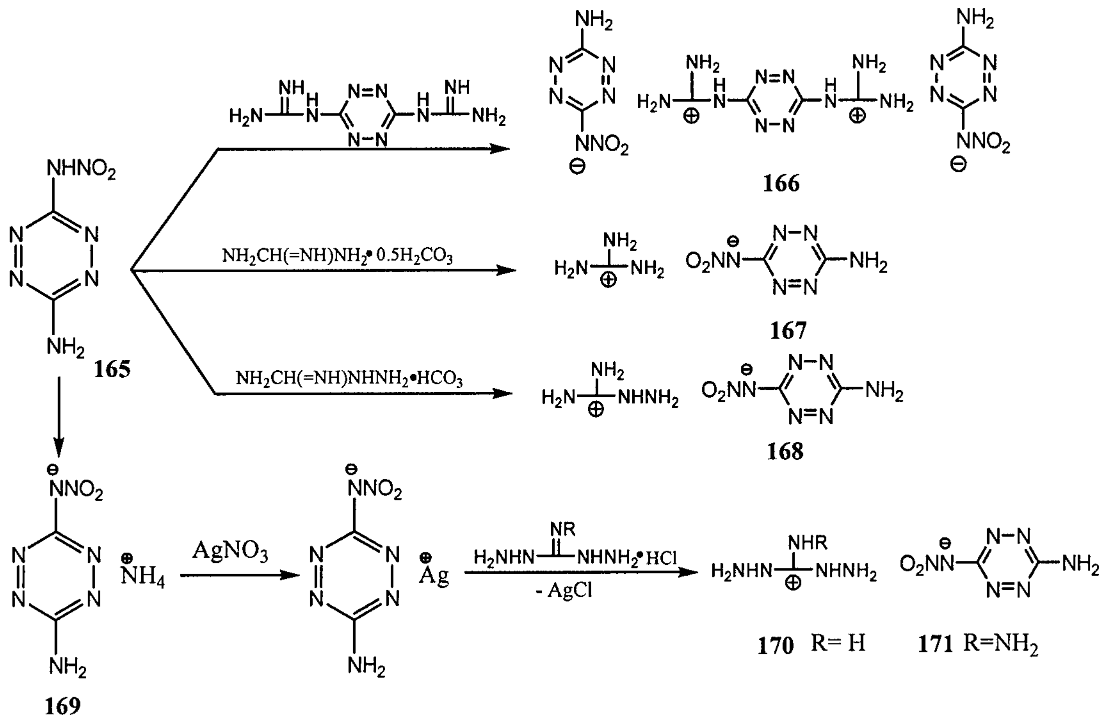
Figure 17. A thermal ellipsoid (30%) drawing of **164b**. b) A ball and stick packing diagram of one layer of **164b** viewed down the a axis. Dashed lines indicate strong hydrogen bonding.

o. 3-Amino-6-nitroamino-tetrazine (ANAT)-based energetic salts.[42]

Recently there has been considerable study of energetic materials based on 1,2,4,5-tetrazine heterocycles. These compounds derive their energy not only from a combination of positive heats of formation and generation of large volumes of N_2 with high order of energy release, but also as a result of high crystal densities. Such properties are important in energetic materials applications. Among them, 3-amino-6-nitroamino-tetrazine (ANAT) **165** has attractive energetic properties. In nitramines, a recently introduced class of organic energetic nitrates, the nitroamino group plays an important role because of the presence of an energetic site and acidic proton making it possible for nitroamino-containing compounds to form corresponding salts. The nitramino group substantially improves the oxygen balance of the corresponding derivatives and eventually results in a higher exothermicity of combustion and detonation processes. The syntheses of the energetic salts **166-171** were easily accomplished by reacting ANAT with one equivalent of guanidine carbonate, aminoguanidine bicarbonate, 3, 6-diguanidine tetrazine, aqueous ammonia, or its silver salt with diaminoguanidine chloride, and triaminoguanidine chloride (Scheme 19). All of the salts were recovered as highly crystalline materials in excellent yields and purities. DSC and TGA studies revealed a family of very stable salts which decompose exothermically upon melting. All of the new salts have relatively high melting points for simple heterocyclic salts, which most likely can be attributed to the high basicity of guanidine or ammonia as well as the extent of crystalline phase hydrogen bonding.

The heats of formation for compounds **165-171** were calculated and are summarized in Table 16. The heat of formation of compound **166** was calculated as +1088.8 kJ/mol. The calculated heats of formation for 3,6-diguanidine tetrazine nitrate **172** and 3,6-diguanidine tetrazine perchlorate **173** are in good agreement with the experimental values of -255kJ/mol and the estimated value of -125 kJ/mol, respectively. This is impressive, considering that the heat of formation of 3,6-diguanidine tetrazine itself is reported to be 197 kJ/mol - a clear indication of the degree of energy

Scheme 19



imparted to the overall molecule by the ANAT anion. Other compounds were also found to have high heats of formation. Salt **167** has the highest thermal stability decomposing at 248.1°C.

The detonation pressures (P) and detonation velocities (D) were calculated based on the traditional Chapman-Jouget thermodynamic detonation theory (Table 16). For compounds **165-171**, the calculated detonation pressures lie in the range between P = 20.9 GPa [**166,** comparable to tetryl (2,4,6-trinitrophenylmethyl-nitramine), P= 22.6 GPa] [26] and P = 28.9 GPa [**168**, comparable to PETN (pentaerythritol tetranitrate) for which P = 31.0 GPa].[26] Detonation velocities are in the range between D = 7546 m s^{-1} (**166**, comparable to TATB (1,3,5-triamino-2,4,6-trinitrobenzene), D = 7660 m s^{-1}) [26] and D = 8898 m s^{-1} (**168**, comparable to RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), D = 8754 m s^{-1}). These properties make these high-nitrogen materials attractive candidates for energetic materials applications.

Table 16. Structure and properties of energetic salts with ANAT anion

No.	Td[a] (°C)	Density (g/cm^3)	H_L [b]	$\Delta_f H_m$ [b°]	P[c]	D[d]
165	164.0	1.82	-	441.0[e]	-	-
166	232.3	1.56	1354.5	1088.8	20.9	7546
167	248.1	1.62	567.6	340.7	23.3	8169
168	205.4	1.71	494.8	443.2	28.9	8898
169	174.0	1.63	526.3	370.0	26.6	8448
170	147.7	1.56	475.4	564.2	23.9	8258
171	163.5	1.59	470.5	671.5	26.1	8582
172[f]	-	1.72	1555.0	-252.5	25.6	8160
173[g]	-	1.90	1512.7	-164.8	30.9	8593

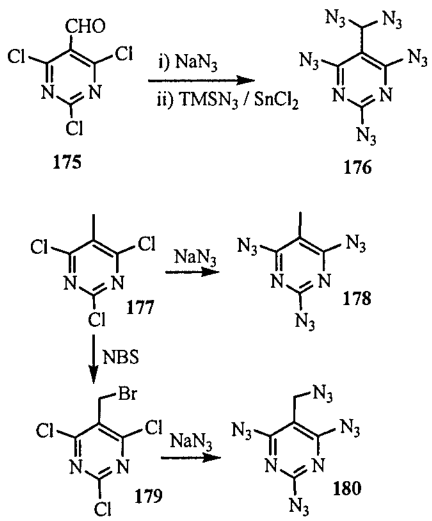
[a] onset of decomposition; [b] kJ/mol; [c]detonation pressures (GPa); [d]detonation velocities (m s^{-1}); [e]calculated heat of formation in the gas phase; [f] 3,6-diguanidine tetrazine nitrate; [g] 3,6-diguanidine tetrazine perchlorate.

p. Polyazidopyrimidines: High-Energy Compounds and Precursors to Carbon Nanotubes.[43]

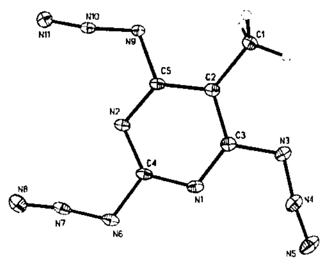
Heterocycles based on geminal diazido compounds had not been reported. We prepared penta(azido)pyrimidine **176** starting from 5-carboxyaldehyde-2,4,6-triazidopyrimidine, **174a** (Scheme 20).

The best yield can be achieved by first substituting the three chlorine atoms on the pyrimidine ring with azide ion; then transforming the aldehyde into geminal diazido using $TMSN_3/SnCl_2$. Remarkably, this pentaazido- compound is a liquid at room temperature with a melting point at ~ -48 °C and has good thermal stability up to ~179 °C. It is noteworthy that **176** can be purified by column chromatography and routine handling while avoiding external heating. This suggests that **176** is not as detonation sensitive as 3,6-diazido-1,2,4,5-tetrazine **174a**. *However, extreme care is absolutely necessary.*

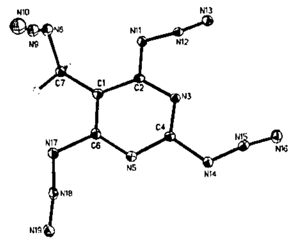
Scheme 20



For comparison purposes, triazido-, and tetrazido-pyrimidine derivatives (**178** and **180,** respectively) were prepared as outlined in Scheme 20. The solid state structures of these two compounds were established by single crystal X-ray analysis. Compound **178** is perfectly planar and packs in sheets similar to the packing in **174b**. There is no molecular overlap between sheets. Compound **180** is also planar and packs in layers. However, in **180**, the molecules have significant overlap with the adjacent layer. The layers are also further apart (3.19 Å), as the steric bulk of the methyl group prevents closer association. There are no significant intermolecular interactions in either **174b** or **178**. The structure of **180** is quite different. In this case, the addition of another alkyl azido group creates many changes. The packing no longer displays flat planar sheets, but stacks along the a axis. These stacks are composed of two alternating molecules. The gap between the molecules in these stacks is ~3.26 Å at the widest with 10° angles between the heterocycles. There are also weak non-classical hydrogen bonds between the methylene group and terminal azido nitrogen atoms, both within the stack (C7 – N13, ca 3.31Å) and between the stacks (C7 – N19, ca. 3.41Å). This compound was difficult to crystallize and has disorder of the alkyl azido group as well as rotational twinning (Figure 18).



178



180

Figure 18. Thermal ellipsoid plot (30%) of **178** and **180**. Hydrogen atoms have been included but not labeled.

The melting point of the triazido-analogue **178** is 103 °C, while the addition of one extra alkyl azido group **180** reduces the melting point drastically by ~ 80 °C to 22.5 °C (Table 17). The introduction of a fourth azido group does not result in any obvious decrease in thermal stability. The presence of a fifth azido group led to a decrease in the melting point by an additional 70 °C, with just a slight decrease in thermal stability (Table 17). Theoretical calculations show that these compounds exhibit highly promising

Table 17. Physical properties of polyazido compounds

Compd.	Density (g cm^{-3})	m.p. (°C)	T_d (°C, DSC)	$\Delta_f H^o_{298}$[a] (kJ mol^{-1})
174a	1.72	130	130	1121.7[b]
174b	1.72	94	180	1136.0[c]
176	1.71	-48	179	1807.1
179	1.55	103	195	1087.4
180	1.65	22.5	193	1452.7
182[d]	-	-	-	2192.0

[a]calculated value in gas phase; [b] $\Delta_f H^o_{298}$ (solid) = 1101 kJ mol^{-1}; [c] $\Delta_f H^o_{298}$ (solid) = 1050 kJ mol^{-1}; [d] 5-triazidomethyl-2,4,6-triazidopyrimidine

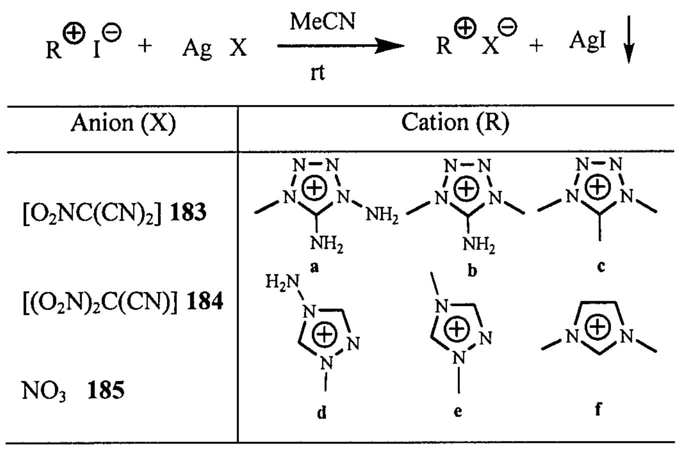
energetic properties.

q. Heterocyclic-Based Nitrodicyanomethanide and Dinitrocyanomethnide Salts.[48]

The nitrate and dinitramide salts of heterocyclic cations are well investigated owing to easier availability and safety of inorganic starting materials. In general, dinitramide salts exhibit more superior properties than their nitrate analogues owing to the bulky molecular structure and higher energetic content of that anion. In our continuing efforts to seek energetic ionic liquids, we became interested in a nitrate pseudochalcogen analogue, nitrodicyanomethanide $[O_2NC(CN)_2]^-$ since theoretical and laboratory investigation revealed significant similarity in their electronic structures, electrochemical and ligation properties. The electron-withdrawing NO_2 and CN groups can stabilize the carbanion and deliver their energy characteristics to the resultant salts. In addition, the bulky structure tends to result in salts with lower melting points. Some metal and ammonium salts of the anion have been reported, but the heterocycle-based salts were seldom investigated despite the fact that heterocyclic ring system usually confers a high density, thermal stability, high nitrogen content, high volume of detonation products and insensitivity to impact. We synthsized and characterized a series of heterocycle-based energetic salts with $[O_2NC(CN)_2]^-$ and $[(O_2N)_2C(CN)]^-$ anions.

The nitrodicyanomethanide (**183a–f**) and dinitrocyanomethanide (**184a–f**) salts were readily prepared through metathesis reactions between equivalent silver (I) salts and iodide salts in MeCN (Scheme 20). The cation choice was made in order to establish the broad relative potential to form energetic ILs and to comprehensively evaluate their performance.

Scheme 21



Phase transition temperatures (midpoints of glass transition and/or melting points) were determined by differential scanning calorimetry (DSC) (Table 18). As anticipated, the anion exhibits a major influence on the phase transition temperature. The melting points of dinitrocyanomethanide salts (**184a–f**) are higher than those of nitrodicyanomethanide analogues (**183a–f**). It should be pointed out that 1,4-dimethyl-5-aminotetrazolium-based salts (**183b, 184b**) have

Table 18. Properties of Energetic Salts

compd	T_m[a] (°C)	T_d[b] (°C)	D_{exptl}[c] (g/cm^3)	d_{calcd}[d] (g/cm^3)	$\Delta_f H_{cation}$ (kJ/mol)	$\Delta_f H_{anion}$ (kJ/mol)	$\Delta_f H_{lat}$[e] (kJ/mol)	$\Delta_f H_m$[f] (kJ/mol)	$\Delta_f H$[g] (kJ/g)
183a	72	176	1.48	1.52	998.0	32.2	479.9	550.3	2.44
183b	94	260	1.41	1.45	885.5	"	474.5	443.2	1.98
183c	50	240	1.38	1.39	844.8	"	472.4	404.6	1.81
183d	59[h]	238	–	1.46	895.6	"	487.4[j]	440.4[j]	2.11
183e	61	237	1.39	1.39	756.9	"	481.8	307.3	1.48
183f	63	327	1.31	1.36	652.1	"	475.1	209.2	1.01
184a	116	182	1.64	1.62	998.0	-127.7	482.1	388.2	1.58
184b	–[i]	145	1.56	1.55	885.5	"	476. 4	281.4	1.15
184c	89	215	1.49	1.48	844.8	"	471.3	245.8	1.01
184d	–54	221	–	1.56	895.6	"	484.2[j]	283.7[j]	1.36
184e	89	206	1.49	1.49	756.9	"	479.1	150.1	0.66
184f	79	267	1.47	1.45	652.1	"	477.9	46.5	0.20
185b	178	206	1.51	1.53	885.5	-307.9	514.2	63.4	0.36
185c	–[i]	199	1.38	1.45	844.8	"	503.0	33.9	0.19
185e	63	197	1.38	1.45	756.9	"	515.0	-66.0	-0.41
185f	71	283	1.36	1.40	652.1	"	513.8	-169.6	-1.07

[a] Melting point; [b] Thermal degradation temperature; [c] Experimental density; [d] Calculated density; [e] Calculated molar lattice energy; [f] Calculated molar enthalpy of formation; [g] Calculated enthalpy of formation in kJ/g [h] Glass transition temperature; [i] Decomposes before melting; [j] Based on calculated density.

higher melting points than their analogues, which may be ascribed to their high symmetry and extensive hydrogen bonding interactions between cation and anion. The melting point of **184a** is above 100 °C which places it outside of the range for an ionic liquid, whereas **184b** decomposed before its phase transition temperature. Interestingly, 1-methyl-4-aminotriazolium-based salts

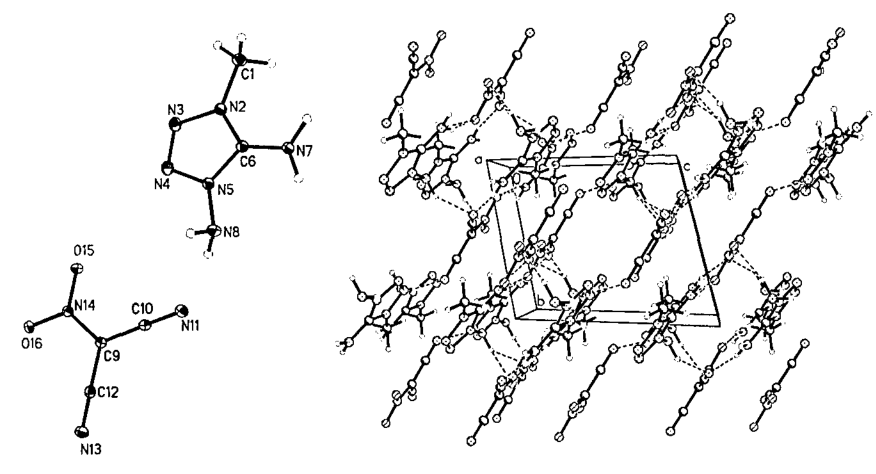
(**183d** and **184d**) are room temperature ionic liquids. With constant anions, the variation in cations has no obvious effect on melting point. The decomposition temperatures of the salts are in the range of 145–327 °C as determined by thermogravimetric analysis (TGA). The lower thermal stability of **184b** is surprising. The 1,3-dimethylimidazolium-based salts have the higher thermal stabilities than their analogues. Noteworthy, the melting point of the 1,5-diamino-4-methyltetrazolium salt **183a** is lower but its thermal stability is higher than nitrate analogue (T_m = 121, T_d = 181 °C). Similar results were found for the remainder of salts.

The densities of the dinitrocyanomethanide and nitrodicyanomethanide salts are in the range of 1.31–1.64 g/cm^3. With the presence of a higher concentration of nitro groups, the opportunity for hydrogen bonding is markedly increased; therefore, it is not surprising that the densities of dinitrocyanomethanide salts are higher than those of its nitrodicyanomethanide analogues. With a constant anion, the effect of cation on density is in the order: 1,5-diamino-4-methyltetrazolium >1,4-dimethyl-5-aminotetrazolium >1,4,5-trimethyltetrazolium ~1,4-dimethyltriazolium > 1,3-dimethylimidazolium. Hence, **184a** and **183f** exhibit the highest density (1.64 g/cm^3) and the lowest density (1.31 g/cm^3), respectively. The densities were also estimated according to our newly tabulated volume parameters, which agreed reasonably with the experimental values within 5 % deviation. The measured densities of **183a** and **184a** are consistent with the densities calculated for X-ray crystal structures.

As shown in Table 18, the nitrodicyanomethanide and dinitrocyanomethanide salts exhibit positive enthalpies of formation with the exception of imidazolium-based salt **184f**. Interestingly, the nitrodicyanomethanide anion has a positive calculated heat of formation (32.2 kJ/mol), which is higher than that of dinitrocyanomethanide (–127.7 kJ/mol) and much higher than that of nitrate (–307.9 kJ/mol). Thus, with constant cations, the enthalpies of formation are in the order: $[O_2NC(CN)_2]^-$ > $[(O_2N)_2C(CN)]^-$ >NO_3^-. This suggests $[O_2NC(CN)_2]^-$ is a promising anion in the field of high energy materials. As anticipated, effect of heterocyclic rings on standard enthalpies of formation of analogous salts is in the order: 1,5-diamino-4-

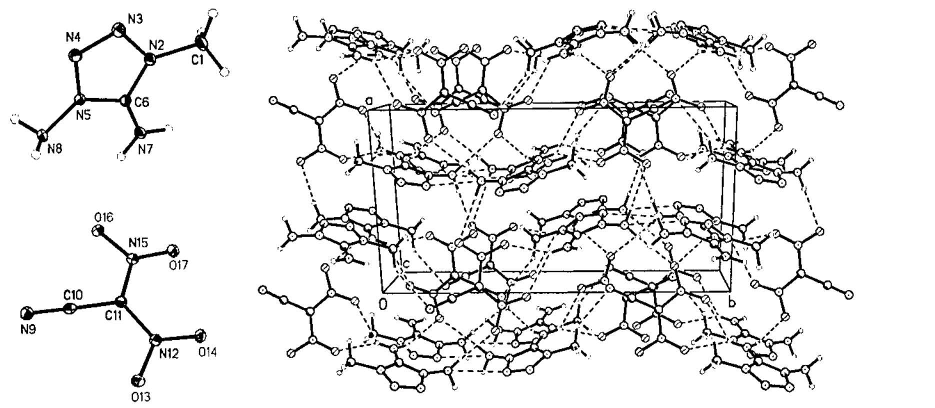
methyltetrazolium > 1,4-dimethyl-5-aminotetrazolium ~ 1-methyl-4-amino-1,2,4-triazolium > 1,4,5-trimethyltetrazolium > 1,4-dimethyltriazolium > 1,3-dimethylimidazolium, which is in keeping with the order of calculated heat of formation for those cations. Among them, **183a** has the highest standard molar enthalpy of formation (550.3 kJ/mol).

183a and **184a** crystallize in the triclinic space group *P-1* and monoclinic space group $P2_1/c$, respectively.. The tetrazolium ring in **183a** and **184a** is almost planar with mean deviations from the ring plane are 0.0012 and 0.0027 Å, respectively. The exocyclic nitrogen atoms (N7 and N8) are out of the plane 0.0199 and 0.0933 Å in **183a**, and 0.0497 and 0.0225 Å in **184a**, respectively. The bond distances and bond angles of the 1,5-diamino-4-methyltetrazolium cation in **183a** and **184a** are close to each other. The anions dinitrocyanomethanide and nitrodicyanomethanide are also planar with mean deviations from the plane are 0.0139 and 0.0198 Å, respectively. The structures are shown in Figures 19 and 20.



a b

Figure 19a. Molecular structure of **183a** with thermal ellipsoids at 50% probability. **b.** Packing diagram of **183a** along *a* axis.



a b

Figure 20a. Molecular structure of **184a** with thermal ellipsoids at 50% probability. **b.** Packing diagram of **184a** along *c* axis.

Nitrodicyanomethanide and dinitrocyanomethanide salts exhibit higher standard enthalpies of formation than their nitrate analogues. We have demonstrated that nitrodicyanomethanide and dinitrocyanomethanide are promising anions toward design and synthesis of higher energy density materials with lower melting points.

r. Rapid and Accurate Estimation of Densities of Room Temperature Ionic Liquids and Salts.[49]

Volume parameters for room temperature ionic liquids (RTILs) and salts were developed. For 59 of the most common imidazolium, pyridinium, pyrrolidinium, tetralkylammonium and phosphonium-based RTILs, the mean absolute deviation (MAD) of the densities is 0.007 g cm^{-3}; for 35 imidazolium-based room temperature salts, the MAD is 0.020 g cm^{-3}; and for 150 energetic salts, the MAD is 0.035 g cm^{-3}. The experimental density (Y) for an alkylated imidazolium or pyridinium-based room temperature ionic liquid is approximately proportional to its calculated density (X) in the solid state: Y = 0.948X - 0.110 (Correlation coefficient: R^2 = 0.998, for BF_4^-, PF_6^-, NTf_2^--containing ionic liquids); Y = 0.934X - 0.070 (Correlation coefficient: R^2 = 0.999, for OTf^-, $CF_3CO_2^-$, $N(CN)_2^-$-containing ionic liquids).

This is a very powerful and rapid method for the estimation of densities. It has been very useful to us in helping us to decide which salts should be synthesized in order to obtain the maximum possible density.

6. Conclusions:

At least 300 new energetic salts have been synthesized and characterized.

1) In general, salts that contain high nitrogen organic anions (with common cations) have higher heats of formation followed by perchlorates > dinitroamides > nitrates. Also, densities decrease in this order.

2) For salts with a common cation, positive heats of formation decrease with substituted tetrazolium > bi(triazolium) > substituted triazolium > substituted imidazolium.

3) Although less energetic, substituted imidazolium salts sometimes are slightly more dense.

4) Guanidinium salts tend to be less dense and have lower heats of formation with nitrate or perchlorate as anion.

5) While some of the new salts have reasonably high positive heats of formation, no thermal or shock sensitivity has been observed. However, direct sensitivity measurements were not made. Some of these compounds may of value in other applications then those sought for this effort. These results are summarized based on cation and/or anion in the APPENDIX (pp. 61-74).

7. Importance of the work to the Air Force:

An amazing array of compounds has been synthesized during the award period. With the exception of sensitivity tests, most of them have been well characterized via density, thermal decomposition and melting point temperature measurement and calculated heat of formation. A large number of these compounds have the potential to be of value in areas where new, stable energetics are required and where those with properties associated with ionic liquids, i. e., low vapor pressure, high thermal and hydrolytic stability, high density, moderate viscosity, etc., can participate effectively by increasing the energy obtained per unit volume.

8. Personnel Supported:

Dr. Hong Xue (postdoctoral fellow), Dr. Chengfeng Ye (postdoctoral fellow), Dr. Ye Gao (postdoctoral fellow), Dr. Yangen Huang (postdoctoral fellow), Jinwi Kim (MS '04), Dr. Chuan-Ming Jin (postdoctoral fellow), Dr. Haixiang Gao (postdoctoral fellow), Sean Arritt (undergraduate), and Crystal Piekarski (undergraduate) have worked on the project. Dr. Brendan Twamley is the campus x-ray crystallographer (no charge for his time but each structure is ~ $100).

9. Publications:

1. Mirzaei, Y.; Twamley, B.; Shreeve, J. M. "Syntheses of 1-Alkyl-1,2,4-Triazoles and the Formation of Quaternary 1-Alkyl-4-Polyfluoroalkyl-1,2,4-Triazolium Salts Leading to Ionic Liquids," *J. Org. Chem.* **2002,** *67*, 9340-9345.

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10. Interactions/Transitions:

Interactions -

a. PI attended the Third Advanced Energetics Technical Exchange in Arlington, VA July 12-14, 2005.

b. PI presented at the 2005 AFOSR Contractors' Meeting in Molecular Dynamics and Theoretical Chemistry (Ionic Liquids section) in Monterey, CA on May 22-24, 2005

c. PI presented at the 17^{th} Winter Fluorine Conference in St. Pete Beach, FL on January 9-14, 2005.

d. PI presented at the 17^{th} International Symposium on Fluorine Chemistry in Shanghai, China on July 24-29, 2005. (2 papers)

e. PI attended the 230^{th} American Chemical Society meeting in WDC on August 28-30, 2005.

f. PI presented at the AFOSR Ionic Liquids Workshop in Tuscaloosa, AL on February 7-8, 2006.

g. PI presented at the 18^{th} International Symposium on Fluorine chemistry in Bremen, Germany on July 29-August 4, 2006.

h. PI presented at the Polynitrogen Workshop in Los Angeles, CA, September 15, 2006.

Transitions -

a. PI involved in an SBIR (OSD06-PR3) proposal (with CFD Research Corporation) which has been awarded (March 2007).

A variety of new compounds but no inventions or patent disclosures.

Honors/Awards: PI now holds a named Professorship – Jean'ne M. Shreeve Professor of Chemistry.

11. APPENDIX

Attached is a Summary Report entitled "Summary of Results for Salts (by anion) which melt in Two Temperature Ranges (<25 °C and >25 °C < 100 °C)." All of the salts fall into the ionic liquid class. All of the materials have been carefully characterized by the usual spectroscopic techniques (NMR, IR, MS), thermal stability (TGA), melting point (DSC) elemental analysis, and density (experimental and calculated). Additionally, heat of formation and detonation properties (detonation pressure and velocity, and specific impulse) have been calculated using Gaussian03 and Cheetah 4.0 methodologies.

The Summary Report is accompanied by the values for each of the salts as a function of the anion. It is difficult to draw conclusions strictly from the single summary sheet with more being gained by leafing through the data for each of the salts. For liquids with melting points < 25 °C, perchlorates, 3,5-dinitro-1,2,4-triazolates and 5-nitro-tetrazolates have higher densities which of course lead to better specific impulse values. While nitrates tend to exhibit greater thermal stability (T_d), they lose with respect to other properties, viz., decomposition pressure, decomposition velocity, and specific impulse.

For salts which melt >25 < 100 °C, with the exception of a nitrate with a diazido-containing cation (23b) which exhibits a detonation pressure of 32 Gpa (RDX = 34) and decomposition temperature of 97 °C (the analogous perchlorate salt has a calculated detonation pressure of 40 Gpa – it is very unstable – it blew up when we synthesized it), the nitrate salts are the least meritorious. The densities of these salts are in general higher than their lower melting analogues.

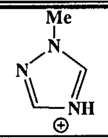
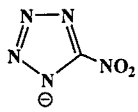
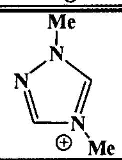
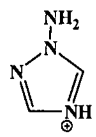
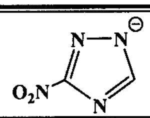
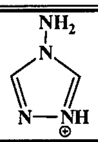
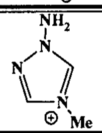
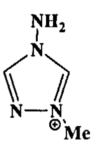
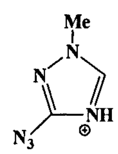
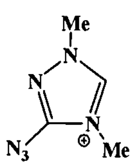
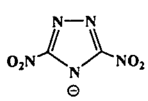
Also attached is a "Summary of Results for Salts (by cation) which melt in Two Temperature Ranges (<25 °C and >25 °C < 100 °C)."

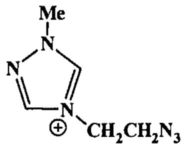
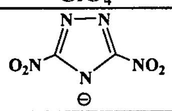
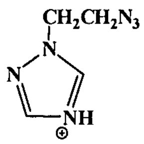
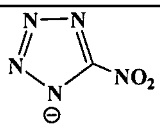
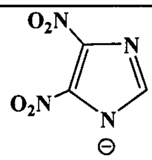
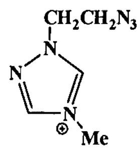
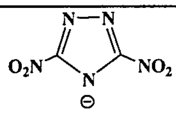
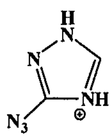
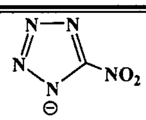
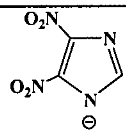
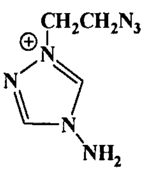
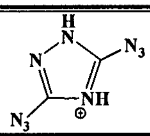
Conclusions

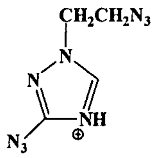
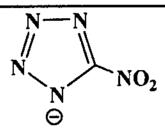
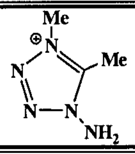
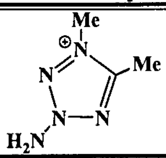
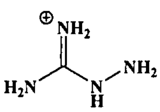
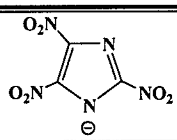
Overall perchlorate is the anion of choice in either ionic liquids melting above or below 25 °C. Perchlorate contributes most positively to the decomposition temperature, density, most often for heat of formation (always when compared with nitrate but rarely with nitroheterocyclic anions) Perchlorate also wins for decomposition pressure, decomposition velocity and specific impulse.

The most positive information gained is that the use of polynitro heterocyclic anions, while not strictly competitive with perchlorate, do appear to be superior to other anions. Of course, they are more environmentally friendly than perchlorates. Unfortunately we have not synthesized large numbers of dinitramides ($N(NO_2)_2^-$) and the salts that we have made do not fall into these temperature ranges or have very low densities. The polynitro heterocycles include 4,4-dinitroimidazolates, 3,5-dinitrotriazolates and trinitroimidazolates.

Summary of Results for Salts (by cation) – Blue (MP > 25 °C < 100 °C); Red (MP < 25 °C)

Cation	Anion	No.	Formula	Tm (Tg) °C	Td °C	D g/cm^3	ΔH°_f (kJ/mol)	P Gpa	vD m/s	I_{sp} s
		17b	$C_4N_8H_6O_2$	62	163	1.52	403	20	7533	214
	ClO_4^-	19a	$C_4N_3H_8O_4Cl$	(-34)	97	1.63	-30	22	7447	214
	NO_3^-	18a	$C_4N_4H_8O_3$	1	160	1.45	-73	16	7043	196
		16b	$C_4N_8H_5O_2$	64	198	1.50	834	24	7560	261
	ClO_4^-	2b	$C_2N_4H_5O_4Cl$	83	208	1.81	125	31	8477	263
	NO_3^-	1b	$C_2N_5H_5O_3$	69	181	1.64	77	26	8025	239
	NO_3^-	1a	$C_3N_5H_7O_3$	(-62)	217	1.51	46	21	7588	215
	NO_3^-	17a	$C_3N_5H_7O_3$	(-60)	221	1.55	58	22	7451	216
	ClO_4^-	3b	$C_3N_4H_7O_4Cl$	86	259	1.66	107	25	7661	244
	NO_3^-	9b	$C_3N_7H_5O_3$	66	139	1.63	309	24	7825	234
	ClO_4^-	10b	$C_3N_6H_5O_4Cl$	55	147	1.66	353	25	7789	257
		8a	$C_6N_{11}H_7O_4$	(-22)	118	1.60	599	23	7700	225
	ClO_4^-	7b	$C_4N_6H_7O_4Cl$	68	147	1.67	324	25	7637	237
	NO_3^-	8b	$C_4N_7H_7O_3$	98	129	1.53	283	21	7597	221

	NO_3^-	11a	$C_5N_7H_9O_3$	(-56)	143	1.45	283	18	7256	214
	ClO_4^-	19b	$C_5N_6H_9O_4Cl$	63	152	1.59	322	22	7535	228
		7a	$C_7N_{11}H_9O_4$	(-43)	179	1.71	574	23	7780	217
	ClO_4^-	12a	$C_4N_6H_7O_4Cl$	(-56)	150	1.61	339	25	7461	239
		13a	$C_5N_{11}H_7O_2$	(-42)	164	1.51	744	20	7634	227
		21b	$C_7N_{10}H_8O_4$	85	140	1.62	539	22	7275	217
	NO_3^-	20b	$C_4N_7H_7O_3$	99	170	1.60	288	22	7572	222
	NO_3^-	9a	$C_5N_7H_9O_3$	(-57)	119	1.49	274	19	7437	213
	ClO_4^-	10a	$C_5N_6H_9O_4Cl$	(-52)	192	1.60	316	22	7571	228
		18b	$C_7N_{11}H_9O_4$	88	189	1.61	576	22	7352	217
		4a	$C_3N_{11}H_3O_2$	(-35)	161	1.53	801	25	7650	249
		14b	$C_5N_{10}H_4O_4$	92	158	1.70	593	25	7814	235
	ClO_4^-	16a	$C_4N_7H_8O_4Cl$	(-46)	218	1.63	451	25	7706	246
	NO_3^-	22b	$C_4N_8H_8O_3$	70	153	1.57	405	22	7698	231
	NO_3^-	23b	$C_2N_{10}H_2O_3$	97	136	1.70	713	32	8739	276
	ClO_4^-	24b	$C_2N_9H_2O_4Cl$			1.84	753	40	9075	275

	NO_3^-	14a	$C_4N_{10}H_6O_3$	(-54)	142	1.58	652	24	7738	242
		15a	$C_5N_{14}H_6O_2$	(-46)	141	1.52	1099	22	7791	242
	NO_3^-	3a	$C_3N_6H_8O_3$	(-59)	170	1.50	146	22	7538	223
	ClO_4^-	5b	$C_3N_5H_8O_4Cl$	51	182	1.71	184	27	8046	247
	NO_3^-	6b	$C_3N_6H_8O_3$	94	173	1.54	132	22	7722	222
		25b	$C_4N_9H_7O_6$	81	253	1.75	44	28	8197	232

Summary of Results for Salts (by anion) which melt in Two Temperature Ranges (<25 °C and >25 °C)

Salts – Liquids at <25 °C

	T_d[a]	Density	heat of formation	P[b]	vD[c]	I_{sp}[d]
	°C	g/cm^3	kJ/mol	Gpa	m/s	s
Nitrate (7)	119-242	1.45-1.58	-73 – 283	16-22	7043-7621	196-223
Perchlorate (4)	97-218	1.60-1.63	-30 – 451	22-25	7461-7706	214-246
5-Nitro-tetrazolate (5)	141-164	1.40-1.53	719 – 801	16-25	7093-7656	218-249
3,5-Dinitro-1,2,4-triazolate (2)	118-179	1.60-1.71	574 – 599	23	7700-7780	217-225

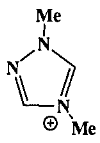
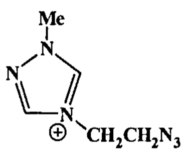
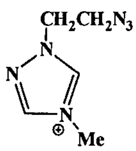
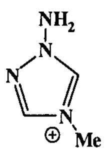
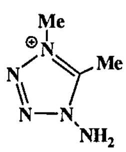
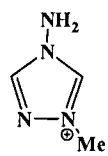
[a] Decomposition temperature; [b] Detonation pressure; [c] Detonation velocity; [d] Specific impulse

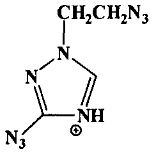
Salts – Liquids at >25 °C < 100 °C

	T_d[a]	Density	heat of formation	P[b]	vD[c]	I_{sp}[d]
	°C	g/cm^3	kJ/mol	Gpa	m/s	s
Nitrate (8)	129-181	1.50-1.70	132 – 713	21-32	7538-8739	221-276
Perchlorate (10)	147-259	1.59-1.84	107 – 353	22-40	7535-9075	228-275
5-Nitro-tetrazolate (1)	163	1.52	403	20	7533	214
3,5-Dinitro-1,2,4-triazolate (1)	189	1.61	576	22	7352	217
4,5-Dinitro-imidazolate (3)	140-158	1.60-1.70	539-593	22-25	7275-7814	217-235
3-Nitro-1,2,4-triazolate (1)	198	1.50	834	24	7560	261
2,4,5-Trinitro-imidazolate (1)	253	1.75	44	28	8197	232

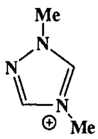
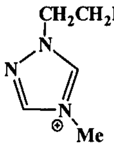
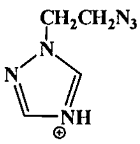
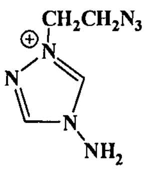
[a] Decomposition temperature; [b] Detonation pressure; [c] Detonation velocity; [d] Specific impulse

Salts - Liquids at <25 °C (by anion)

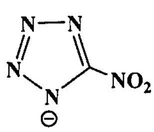
Formula	Tm(Tg) °C	Td °C	density (g/cm^3)	heat of formation (kJ/mol)	P Gpa	νD m/s	I_{sp} s
Nitrate NO_3^-							
18a $C_4N_4H_8O_3$	1	160	1.45	-73	16	7043	196
							
11a $C_5N_7H_9O_3$	(-56)	143	1.45	283	18	7256	214
							
9a $C_5N_7H_9O_3$	(-57)	119	1.49	274	19	7437	213
							
1a $C_3N_5H_7O_3$	(-62)	217	1.51	46	21	7588	215
							
3a $C_3N_6H_8O_3$	(-59)	170	1.50	146	22	7538	223
							
17a $C_3N_5H_7O_3$	(-60)	221	1.55	58	22	7451	216
							

14a $C_4N_{10}H_6O_3$	(-54)	142	1.58	652	24	7738	242
							

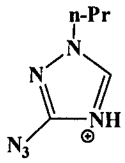
Perchlorate ClO_4^-

19a $C_4N_3H_8O_4Cl$	(-34)	97	1.63	-30	22	7447	214
							
10a $C_5N_6H_9O_4Cl$	(-52)	192	1.60	316	22	7571	228
							
12a $C_4N_6H_7O_4Cl$	(-56)	150	1.61	339	25	7461	239
							
16a $C_4N_7H_8O_4Cl$	(-46)	218	1.63	451	25	7706	246
							

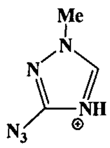
5-Nitrotetrazolate



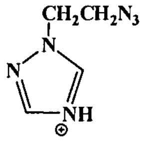
6a $C_6N_{11}H_9O_2$	(-45)	153	1.40	719	16	7093	218



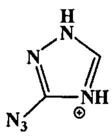
5a $C_4N_{11}H_5O_2$ (-38) 141 1.45 769 19 7395 237



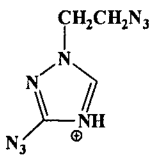
13a $C_5N_{11}H_7O_2$ (-42) 164 1.51 744 20 7634 227



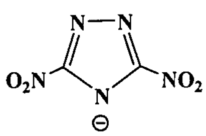
4a $C_3N_{11}H_3O_2$ (-35) 161 1.53 801 25 7650 249



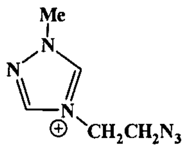
15a $C_5N_{14}H_6O_2$ (-46) 141 1.52 1099 22 7791 242



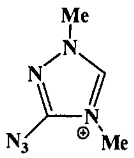
3,5-Dinitro-1,2,4-triazolate



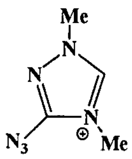
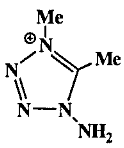
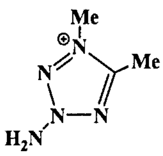
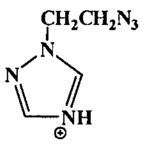
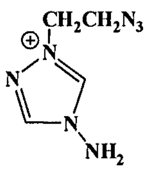
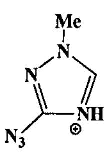
7a $C_7N_{11}H_9O_4$ (-43) 179 1.71 574 23 7780 217

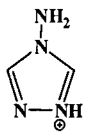


8a	$C_6N_{11}H_7O_4$	(-22)	118	1.60	599	23	7700	225

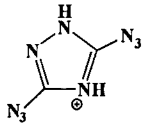


Salts – Melting points >25 °C < 100 °C (by anion)

Formula	Tm(Tg) °C	Td °C	density (g/cm^3)	heat of formation (kJ/mol)	P Gpa	vD m/s	I_{sp} s
Nitrate NO_3^-							
8b $C_4N_7H_7O_3$	98	129	1.53	283	21	7597	221
							
12b $C_3N_6H_8O_3$			1.50	146	22	7538	223
							
6b $C_3N_6H_8O_3$	94	173	1.54	132	22	7722	222
							
20b $C_4N_7H_7O_3$	99	170	1.60	288	22	7572	222
							
22b $C_4N_8H_8O_3$	70	153	1.57	405	22	7698	231
							
9b $C_3N_7H_5O_3$	66	139	1.63	309	24	7825	234
							
1b $C_2N_5H_5O_3$	69	181	1.64	77	26	8025	239

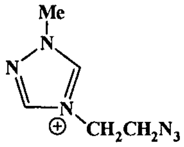


23b $C_2N_{10}H_2O_3$ 97 136 1.70 713 32 8739 276

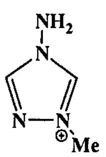


Perchlorate ClO_4^-

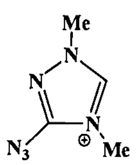
19b $C_5N_6H_9O_4Cl$ 63 152 1.59 322 22 7535 228



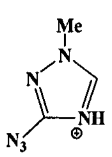
3b $C_3N_4H_7O_4Cl$ 86 259 1.66 107 25 7661 244



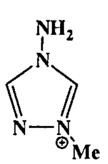
7b $C_4N_6H_7O_4Cl$ 68 147 1.67 324 25 7637 237



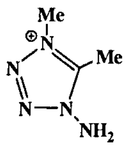
10b $C_3N_6H_5O_4Cl$ 55 147 1.66 353 25 7789 257



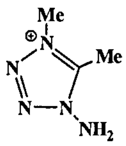
11b $C_3N_4H_7O_4Cl$ 86 259 1.72 107 26 7880 244



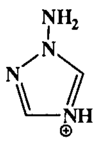
13b $C_3N_5H_8O_4Cl$ 51 1.71 107 26 7969 237



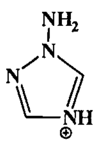
5b $C_3N_5H_8O_4Cl$ 51 182 1.71 184 27 8046 247



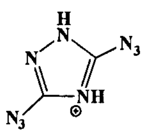
2b $C_2N_4H_5O_4Cl$ 83 208 1.81 125 31 8477 263



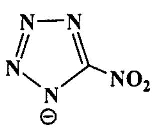
4b $C_2N_4H_5O_4Cl$ 91 235 1.80 127 31 8442 264



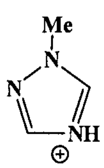
24b $C_2N_9H_2O_4Cl$ 1.84 753 40 9075 275



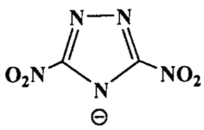
5-Nitrotetrazolate



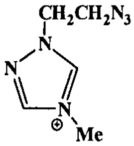
17b $C_4N_8H_6O_2$ 62 163 1.52 403 20 7533 214



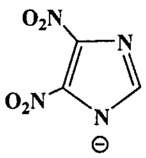
3,5-Dinitro-1,2,4-triazolate



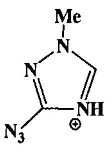
18b $C_7N_{11}H_9O_4$	88	189	1.61	576	22	7352	217



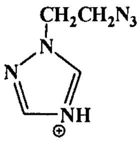
4,5-Dinitroimidazolate



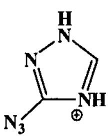
15b $C_6N_{10}H_6O_4$	80	145	1.60	560	22	7587	225



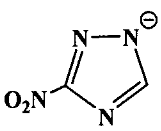
21b $C_7N_{10}H_8O_4$	85	140	1.62	539	22	7275	217



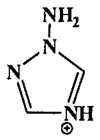
14b $C_5N_{10}H_4O_4$	92	158	1.70	593	25	7814	235



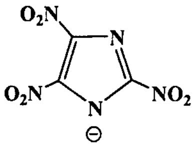
3-Nitro-1,2,4-triazolate



16b $C_4N_8H_5O_2$	64	198	1.50	834	24	7560	261



2,4,5-Trinitroimidazolate



25b	$C_4N_9H_7O_6$	81	253	1.75	44	28	8197	232